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MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria

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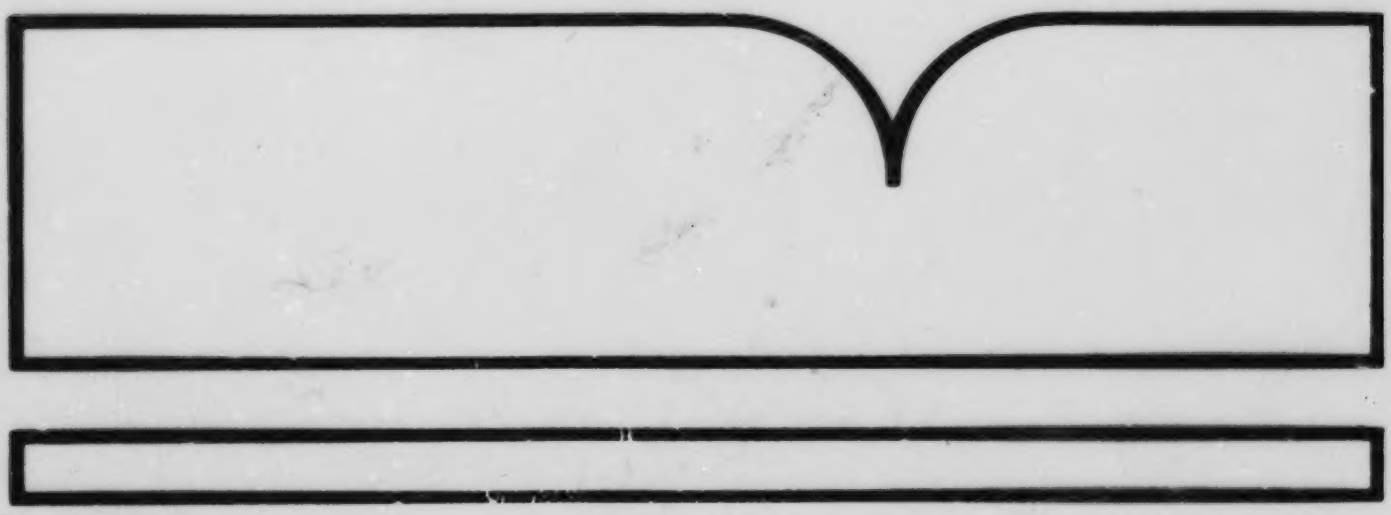

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MINTEQ--A COMPUTER PROGRAM FOR CALCULATING AQUEOUS GEOCHEMICAL EQUILIBRIA

by

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MINTEQ is a computer program for computation of geochemical equilibria. MINTEQ was developed for incorporation into the Metals Exposure Analysis Modeling System (MEXAMS), a modeling system for the assessment of the fate and migration of selected priority pollutant metals in aquatic systems. MINTEQ combines the best features of two existing geochemical models MINEQL and WATEQ3. The mathematical structure was taken from MINEQL. The WATEQ3 features were added to this basic structure. The main features obtained from WATEQ3 are the well referenced thermodynamic data base, temperature correction of equilibrium constants using either the Van't Hoff relationship or analytical expressions for the equilibrium constants as a function of temperature and ionic strength correction using either the extended Debye-Huckel equation or the Davies equation. Six different adsorption algorithms: an "activity" Kd, an "activity" Langmuir equation, an "activity" Freundlich equation, an ion exchange algorithm, a constant capacitance surface complexation model, and the triple layer surface complexation model. In addition, a large number of user oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different analytical inputs were incorporated.

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The MINTEQ computer code has been tested against other computer programs to verify its computational accuracy. Nevertheless, errors in the code are possible. The U.S. Environmental Protection Agency assumes no liability for either misuse of the model or for errors in the code. The user should perform verification checks of the code before using it.

FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

Concern about environmental exposure to heavy metals has increased the need for techniques to predict the behavior of metals entering natural waters as a result of the manufacture, use, and disposal of commercial products. Previously, mathematical models have been developed to provide data on aquatic geochemistry, including metals speciation at equilibrium. The modeling technique described in this manual combines the best elements of two of these models and permits the user to examine what species of a metal are likely to be present under different chemical conditions in a water body. Because different species of a metal cause different biological effects, this model should help users better relate metals concentration and aquatic chemistry to observed effects.

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ABSTRACT

MINTEQ is a computer program for computation of geochemical equilibria. MINTEQ was developed for incorporation into the Metals Exposure Analysis Modeling System (MEXAMS) a modeling system for the assessment of the fate and migration of selected priority pollutant metals in aquatic systems.

MINTEQ combines the best features of two existing geochemical models, MINEQL and WATEQ3. The mathematical structure was taken from MINEQL. The WATEQ3 features were added to this basic structure. The main features obtained from WATEQ3 are the well referenced thermodynamic data base, temperature correction of equilibrium constants using either the Van't Hoff relationship or analytical expressions for the equilibrium constants as a function of temperature, and ionic strength correction using either the extended Debye-Huckel equation or the Davies equation. Six different adsorption algorithms were added: 1) an "activity" K_d, 2) an "activity" Langmuir equation, 3) an "activity" Freundlich equation, 4) an ion exchange algorithm, 5) a constant capacitance surface complexation model, and 6) the triple layer surface complexation model. In addition, a large number of user oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different ana ytical input units were incorporated.

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List of Abbreviations and Symbols

A - Davies equation A parameter

A_d - Debye-Huckel A parameter

a_i - Debye-Huckel ion size parameter

$a_{(i,j)}$ - stoichiometric coefficient of component j in species i

α_1 - constant used in computing log γ for neutral species

A^Z - ion of charge Z

B - conversion factor for coulombs of charge per square meter into moles of charge per liter

B_d - Debye-Huckel B parameter

b_i - Debye-Huckel parameter which allows for the decrease in solvent concentration in concentrated solutions

C - total dissolved concentration

C_i - concentration of species i

C_1 - capacitance between 'o' and 'b' planes in the triple layer model.

C_2 - capacitance between 'b' and 'd' planes in the triple layer model.

C' - capacitance of the double layer in the constant capacitance model.

C_s - concentration of solid in suspension

E_c - total excess equivalents of acid consumed by carbonate containing species over the stoichiometry of carbonate in each species.

E_N - noncarbonate alkalinity

ε - dielectric constant

ε_o - permittivity of free space.

F - Faraday's constant

f_i - carbonate alkalinity factor for species i

γ_i - activity coefficient for species i

I - ionic strength

$\underline{J}$ - Jacobian matrix

$^*K$ - equilibrium constant for adsorption reactions written in terms of the neutral sites (XOH) rather than the charged site (SO^-).

K_d - distribution coefficient

K_d^{act} - "activity" K_d

K_{ex} - equilibrium constant for ion exchange reactions

K_F - Freundlich constant

K_F^{act} - "activity" Freundlich constant

K_i - equilibrium constant for reaction i

K_L - Langmuir adsorption constant

K_L^{act} - "activity" Langmuir constant

K_r^o - equilibrium constant for reaction at 298.15°K

λ - F/RT

m - total number of aqueous species

M_i - mass of solid phase i

n - total number of components

$1/n$ - Freundlich constant

N_a - Avagadro's number

N_s - surface site density

ψ - electrostatic potential at a designated adsorption plane

q_i - noncarbonate alkalinity factor for species i

R - ideal gas constant

s - number of aqueous species plus number of solid phases

$\underline{S}$ - total mass adsorbed in molal units

$\overline{S}$ - free or unoccupied surface sites

S_A - specific surface area

σ - total charge at a designated adsorption plane

SI - saturation index

S_T - maximum quantity adsorbed in Langmuir isotherm

T_j - total analytical concentration of component j

X_j - activity of component j

Y_j - difference function (relaxed mass balance constraint) for component j

Z_i - charge on species i

Z(j,k) - Jacobian matrix of partial derivatives $\partial Y_j / \partial X_K$.

SECTION 1

INTRODUCTION

This report describes MINTEQ, a computer program for computation of geochemical equilibria. MINTEQ combines the best features of its precursors MINEQL (Westall et al. 1976) and WATEQ3 (Ball et al. 1981). Financial support for the development of MINTEQ has come from several sources. Development of the original WATEQ3 data base (Ball et al. 1981) was done by the United States Geological Survey (USGS). Development of the mathematical structure in MINEQL was supported under an earlier project funded by the Environmental Protection Agency (EPA). Incorporation of the WATEQ3 features and adsorption algorithms into the MINEQL mathematical structure was performed as part of EPA Contract No. 68-03-3089. The objective of this contract was to develop a predictive methodology for the assessment of the migration and fate of priority pollutant metals in aquatic systems. To meet this objective, MINTEQ was coupled with EXAMS, the Exposure Analysis Modeling System, through a user interactive program. The complete geochemical-transport modeling system is called MEXAMS, the Metals Exposure Analysis Modeling System. A separate report entitled MEXAMS - The Metals Exposure Analysis Modeling System provides guidelines for the use of MINTEQ. This report presents the chemical and mathematical concepts embodied in MINTEQ. Since the mathematical structure in MINTEQ is the same as in MINEQL, Westall's (1976) original notation will be used in this report.

MINTEQ provides a great deal of flexibility in the way the user defines the chemistry of the system being modeled. Although one does not need to

master the concepts presented in this report to effectively use MINTEQ, a basic understanding of the program will allow experienced users to solve a very broad range of chemical equilibrium problems. It is recommended that the user begin by reading the report entitled, MEXAMS - The Metals Exposure Analysis Modeling System.

This report is divided into three major sections. The first section describes the equations for computing equilibria with regard to aqueous speciation, adsorption and solid phases. The second section describes the numerical methods employed to solve the chemical equilbrium problem and the third section describes the thermochemical values which constitute the data base.

SECTION 2

CONCLUSIONS

The geochemical model MINTEQ is capable of calculating equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states and precipitation/dissolution. MINTEQ combines the best features of two geochemical precursors; MINEQL and WATEQ3. MINTEQ can solve a much broader range of chemical equilibrium problems than WATEQ3, is more user-oriented than MINEQL, contains a well referenced thermodynamic data base, and contains six different algorithms for calculating adsorption.

MINTEQ, like MINEQL, has a general mathematical approach to solving the chemical equilibrium problem. The general mathematical approach allows MINTEQ to solve a broad range of chemical equilibrium problems.

SECTION 3

RECOMMENDATIONS

The capabilities of MINTEQ would be extended if the thermodynamic data for aqueous species and solid phases of additional elements were added to the data base. Available data in the literature should be critically reviewed and the most accurate values incorporated into the MINTEQ data base. Furthermore, as more reliable thermodynamic data for important aqueous species and solid phases already in the model become available, they should be used to update the data base thereby increasing the overall competency of the model.

MINTEQ does not have a kinetic capability, it is only a thermodynamic equilibrium model. In many environmental systems the equilibrium assumption may not be valid. Kinetics of solid precipitation or dissolution may dominate the geochemistry of the system. Therefore, including kinetics of precipitation/dissolution and of oxidation-reduction would be an important extension.

The elementary ion association models used in MINTEQ for computing activity coefficients and aqueous speciation are not valid for high ionic strength solutions (i.e., ionic strengths equal to or greater than sea water). Higher order ion interaction models described by (Pitzer 1973; Pitzer and Mayorga 1973, Pitzer and Kim 1974) appear to be more reliable at high ionic strengths (Harvie and Weare 1980). Such models should be incorporated into MINTEQ for treating high ionic strength solutions where the ionic strength exceeds approximately 0.7 molal.

SECTION 4

MODEL THEORY

This section describes the formulation of the chemical equilibrium problem in MINTEQ. The equilibrium equations for aqueous speciation, adsorption and solid phases are described.

BASIC FORMULATIONS

The chemical equilibrium problem can be described by a set of mass balance equations, one for each component, and a set of mass action expressions, one for each species. The problem then reduces to solving the non-linear mass action expressions with the linear mass balance equations. This is commonly termed the equilibrium constant approach to the chemical equilibrium problem. There are other formulations of the chemical equilibrium problem that are also possible. As an example, at fixed temperature and pressure the chemical equilibrium problem can also be solved by a direct minimization of the Gibbs free energy or the Helmholtz free energy if the volume and temperature are specified [see Van Zeggeren and Storey (1970)].

The equilibrium constant approach is used in MINTEQ. A basic set of components is chosen and all mass action equations are written in terms of the components [Equation (1)],

$$\gamma_i C_i = K_i \prod_{j=1}^{n} X_j^{a(i,j)} \qquad (1)$$

where

γ_i = activity coefficient for species i

C_i = concentration of species i

K_i = equilibrium constant for reaction i

X_j = activity of component j

$a(i,j)$ = stoichiometric coefficient of component j in species i

n = number of components j.

The mass balance equations can then be written as a summation of the C_i terms (Westall et al. 1976),

$$T_j = \sum_{i=1}^{m} a(i,j)\, C_i \qquad (2)$$

where

T_j = total analytical concentration of component j

m = number of aqueous species.

Equation (2) can be reformulated to make the solution to the chemical equilibrium problem easier to solve by relaxing the mass balance constraint at intermediate iterations (Westall et al. 1976),

$$Y_j = \sum_{i=1}^{m} a(i,j)\, C_i - T_j \qquad (3)$$

where

Y_j = difference function for component j.

The solution is the set of all X_j terms such that all Y_j terms equal zero. The convergence criterion is described in Section 5.

The previous mathematical formulations are defined for systems without solid phases. Solid phases are handled in basically two ways. The first method treats the mass of each solid phase as an independent variable and thereby expands the basic set of unknowns (i.e., the X_j terms) to include a variable M_i for each solid phase. The mass balance equations can then be written,

$$Y_j = -T_j + \sum_{i=1}^{m} a(i,j)\, C_i - \sum_{i=m+1}^{s} a(i,j)\, M_i \qquad (4)$$

where s = number of solid phases plus number of aqueous species. The summation over the M_i terms then represents the mass of component j in solid phases.

This method is used in other geochemical models such as EQ3/EQ6 (Wolery 1979) and PHREEQE (Parkhurst et al. 1980).

The second method for handling solid phases is by what is termed a "transformation of basis." This is the method used in MINEQL and retained in MINTEQ. The transformation of basis reduces the number of independent variables which must be determined and also allows the treatment of different chemical reactions in a mathematically general way. This latter attribute allows MINEQL and MINTEQ to solve a wide range of chemical equilibrium problems. The mathematical description, given in Appendix One in Westall

et al. (1976), will not be reproduced here. Instead, the following example is presented to clarify the approach. Suppose there exists a four component system Ca^{2+}, H^+, CO_3^{2-} and H_2O, and the following reactions occur in aqueous solution.

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad , \qquad \log K_r^o = 12.6 \tag{5}$$

$$Ca^{2+} + H^+ + CO_3^{2-} \rightleftarrows CaHCO_3^+ \quad , \qquad \log K_r^o = 11.33 \tag{6}$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3^0 \quad , \qquad \log K_r^o = 3.15 \tag{7}$$

$$H_2O \rightleftarrows OH^- + H^+ \quad , \qquad \log K_r^o = -13.98 \tag{8}$$

where $\log K_r^o$ is the equilibrium constant for the stated reaction at 298.15°K.

If the solid calcite is now imposed as an equilibrium solid then one of the X_j terms in the calcite dissolution reaction, Equation (9), is eliminated computationally and all the reactions containing that component are rewritten with calcite [$CaCO_3(s)$] as a component (Westall et al. 1976),

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(s) \quad , \quad \log K_r^o = 8.475 \tag{9}$$

As an example, suppose $X_{CO_3^{2-}}$ is eliminated then the reactions would be written as:

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad , \qquad \log K_r^o = 12.6 \tag{10}$$

$$CaCO_3(s) + H^+ \rightleftarrows CaHCO_3^+ \quad , \qquad \log K_r^o = 2.855 \qquad (11)$$

$$CaCO_3(s) \rightleftarrows CaCO_3^o \quad , \qquad \log K_r^o = -5.325 \qquad (12)$$

$$H_2O \rightleftarrows H^+ + OH^- \quad , \qquad \log K_r^o = -13.98 \qquad (13)$$

Since the activity of pure calcite is equal to one, the set of independent variables (X_j terms) is reduced by one. The transformation of basis is completely general and, for example, can be applied to species present at a fixed activity, gases at a fixed partial pressure, solids not present at unit activity, or redox reactions which establish a fixed relationship between components.

Activity Coefficients

The activity is related to the concentration by the activity coefficient (γ). MINTEQ corrects the equilibrium constants for ionic strength by a simple rearrangement of the mass action expressions, thus

$$C_i = \frac{(K_r^o)_i}{\gamma_i} \pi X_j^{a(i,j)} \quad . \qquad (14)$$

The resulting equilibrium constant is termed a "mixed constant" because the species formed in the reaction is in terms of concentration and the components are in terms of activities.

MINTEQ uses two alternate formulations for computing activity coefficients: 1) an extended Debye-Huckel equation which contains two

adjustable parameters (Truesdell and Jones 1974), and 2) the Davies equation (Davies 1962). The extended Debye-Huckel equation,

$$\log_{10} \gamma_i = \frac{-A_d Z_i^2 \sqrt{I}}{1 + B_d a_i \sqrt{I}} + b_i I \qquad (15)$$

where

A_d and B_d are the Debye-Huckel constants which depend upon the dielectric constant and temperature,

Z_i = charge on species i

a_i = ion size parameter

b_i = ion specific parameter which allows for the decrease in solvent concentration in concentrated solutions (Truesdell and Jones 1974)

I = ionic strength.

The A_d and B_d constants are computed as described in Truesdell and Jones (1974). The a_i and b_i parameters were taken directly from the WATEQ3 data base (Ball et al. 1981). The ionic strength is,

$$I = \frac{1}{2} \sum_{i=1}^{m} Z_i^2 C_i \quad . \qquad (16)$$

The a_i and b_i parameters are only available for the major ions and certain trace metals such as Cu and Mn. In cases where a_i and b_i are not available for the species formed in the reaction, MINTEQ defaults to the Davies equation for calculation of single ion activity coefficients,

$$\log \gamma_i = -A\, Z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3\, I\right) \qquad (17)$$

Activity coefficients for neutral aqueous species are represented by (Helgeson 1969),

$$\log \gamma_i = \alpha_1 I.$$

MINTEQ sets α_1 to 0.1 for all neutral aqueous species.

The ion association models used in MINTEQ are not valid in high ionic strength solutions (brines). The ion-interaction models published by Pitzer (1973), Pitzer and Mayorga (1973) and Pitzer and Kim (1974) expand the basic Debye-Huckel equation by adding a series of ion interaction terms. These interaction terms are analogous to virial coefficients for non-ideal gases. Such ion interaction models should be added to MINTEQ before it can be accurately applied to high ionic strength solutions.

Activity of Water

The activity of water is calculated in MINTEQ by the relationship

$$X_{H_2O} = 1 - 0.017 \sum_{i=1}^{m} C_i \qquad (18)$$

where m is the total number of aqueous species. The expression is derived from Raoult's law and is valid only for dilute solutions. The constant 0.017 is

obtained from a plot of the activity of water versus number of solute ions (Garrells and Christ 1965).

Temperature Correction

The equilibrium constants in the MINTEQ data base are valid at 298°K or 25°C. MINTEQ corrects these equilibrium constants to temperatures other than 298°K by using either the Van't Hoff relationship or, whenever available, analytical expressions for log K_r^o as a function of temperature.

The analytical expressions for log K_r^o as a function of temperature are expressed as:

$$\log K_T = A + BT + C/T + D \log_{10}(T) + ET^2 + F/T^2 + G/\sqrt{T} \qquad (19)$$

where T is temperature in degrees Kelvin and A through G are empirically derived coefficients. When analytical expressions for log K with temperature are not available, the Van't Hoff relationship is used. The Van't Hoff relation (Lewis and Randall 1961) takes the form:

$$\log K_T = \log K_{Tr} - \frac{\Delta H_r^o}{2.3\ R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \qquad (20)$$

where T_r is the reference temperature (298.15°K), ΔH_r^o is the enthalpy of reaction, T is the specified temperature and R is the ideal gas constant. Data for the enthalpy of reaction were taken from the WATEQ3 data base (Ball et al. 1981) and will be tabulated in Appendix A.

The Van't Hoff relation assumes that ΔH_r^o is independent of temperature. This assumption is not strictly valid so the Van't Hoff relationship may produce substantial errors at temperatures significantly different from 25°C. Unfortunately, data for $\Delta H_{r,298}^o$ or log K expressions as a function of temperatures are not available for all species in the MINTEQ data base. In such cases, the log $K_{r,298}$ is used at all temperatures. Because of these limitations, applications of MINTEQ should definitely be limited to temperatures less than 100°C.

Alkalinity Correction

Frequently, analytical data are available for total alkalinity but not total inorganic carbon. In such cases, MINTEQ can convert total alkalinity to total inorganic carbon. There are three important steps in the conversion.

The first step is to convert the input alkalinity expressed as carbonate to equivalents. This is simply done by multiplying the input alkalinity value by two since carbonate ion will consume two equivalents of acid per mole, Equation (21).

$$T'_{jj} = 2.0\ T_{CO_3^{2-}} \tag{21}$$

where jj represents CO_3^{2-}, $T_{CO_3^{2-}}$ is the titration alkalinity in molality, and T'_{jj} is the titration alkalinity in equivalents.

The next step is to subtract the difference between the equivalents of acid consumed by a carbonate containing species and the stoichiometry of carbonate in the species. As an example, the following species all would

consume two equivalents of acid per mole, CO_3^{2-}, $PbCO_3^0$, $MgCO_3^0$, and contain only one carbonate ion. This means each species consumes one excess equivalent of acid per mole. This difference must be subtracted from the total alkalinity in equivalents to obtain the correct total inorganic carbon. The number of equivalents of acid consumed per mole of a carbonate containing species is termed the carbonate alkalinity factor. The excess equivalents of acid consumed per mole of carbonate containing species is then,

$$E_C = \sum_{i=1}^{m} C_i \, [f_i - a(i,jj)] \tag{22}$$

where

E_C = excess equivalents of acid

f_i = carbonate alkalinity factor for species i

$a(i,jj)$ = molality of carbonate in species i.

The next step is to subtract the noncarbonate alkalinity. Noncarbonate alklinity results from such species as OH^-, $Al(OH)_4^-$, or HPO_4^{2-} which consume acid during the alkalinity titration but do not contain carbonate. The equivalents of acid consumed by nonarbonate containing species is,

$$E_N = \sum_{i=1}^{m} C_i \, q_i \tag{23}$$

where

E_N = equivalents of noncarbonate alkalinity

q_i = noncarbonate alkalinity factor for species i.

The noncarbonate alkalinity factor is the number of equivalents of H^+ consumed by a noncarbonate containing species if the solution were titrated to approximately pH 4.6.

The final step in computing total inorganic carbon is to add the mass of $H_2CO_3(aq)$. The overall conversion can be summarized,

$$T_{jj} = T'_{jj} - \sum_{i=1}^{m} C_i \left(f_i - a_{(i,jj)}\right) - \sum_{i=1}^{m} C_i q_i + C_{ii} \qquad (24)$$

where

T_{jj} = molality of inorganic carbon

f_i = carbonate alkalinity factor,

q_i = noncarbonate alkalinity factor

C_{ii} = mass of $H_2CO_3(aq)$.

ADSORPTION

MINTEQ contains six algorithms for treating adsorption: an "activity Kd," an "activity Langmuir" isotherm, an "activity Freundlich" isotherm, an ion exchange model and two surface complexation models, the constant capacitance surface complexation model (Huang and Stumm 1973; Schindler et al. 1976; Stumm et al. 1976), and the triple layer surface complexation model (Yates et al. 1974; Davis et al. 1978). This section presents a brief review of each model and an outline of the mathematical formalism used by each model. For further detail on the mathematical formalism of the constant capacitance model and the triple layer model see (Westall 1979a, 1979b; Westall 1980; Westall and Hohl 1980).

The K_d and the Langmuir and Freundlich Isotherms

In this section, the traditional concentration K_d and the Langmuir and Freundlich isotherms will be defined in terms of the total dissolved concentration of the adsorbate. These isotherms and the K_d will then be redefined in terms of the activity of the bare adsorbate ion and the limitations of this treatment of adsorption will be discussed.

The distribution coefficient K_d is defined as the ratio of the amount adsorbed to the amount remaining in solution. This can be conceptualized and written as any other reaction. An example for cadmium is,

$$\overline{S} + Cd_{total} \rightleftarrows \overline{SCd} \tag{25}$$

where $\overline{S}$ represents free or unoccupied surface sites, Cd_{total} = total dissolved cadmium remaining in solution, and $\overline{SCd}$ = adsorbed cadmium in molal units.

The mass action expression for Equation (25) is the common definition of the K_d,

$$\frac{\overline{SCd}}{Cd_{total}} = K_d \tag{26}$$

where the implicit assumption is made that $\overline{S}$ is in great excess with respect to Cd_{total} and the activity of $\overline{S}$ is set to one since with an assumed excess the variability of $\overline{S}$ is negligible.

Activity Langmuir Isotherm

The Langmuir equation can be formulated as,

$$S = \frac{K_L S_T C}{1 + K_L C} \tag{27}$$

where

S = the amount adsorbed in molality

K_L = the Langmuir adsorption constant

C = the total dissolved concentration in solution at equilibrium

S_T = the maximum quantity that can be adsorbed in molality.

Assuming that each adsorbing ion occupies only one adsorption site, then S_T is also equal to the total number of adsorption sites. The Langmuir isotherm has the advantage over the activity K_d in considering a mass balance on surface adsorption sites. The Langmuir equation as formulated in Equation (27) is simply a combination of a mass action expression for adsorption and a mass balance equation for surface sites,(a)

$$C + \overline{S} \rightleftarrows S \quad , \tag{28}$$

$$S_T = \overline{S} + S \quad , \tag{29}$$

(a) Note: In this formulation, competition between ions for surface sites can be readily included by formulating additional mass action expressions [Equation (28)] and then including the adsorbed species in the mass balance [Equation (29)].

where

$\overline{S}$ represents surface sites unoccupied by adsorbate.

If the adsorption data do not conform to a Langmuir plot, the Freundlich equation frequently provides a fit to the data. The Freundlich equation is formulated as,

$$S = K_F C^{1/n} \quad . \tag{30}$$

where K_F and 1/n are constants and C is the equilibrium total dissolved concentration. For cadmium adsorption then,

$$\overline{SCd} = K_F (Cd_{tot})^{1/n} \quad . \tag{31}$$

In this example, if the data conform to a Freundlich isotherm a plot of the logarithm of $\overline{SCd}$ versus the logarithm of the concentration of total Cd in solution at equilibrium (Cd_{tot}) would yield a straight line with slope 1/n and an intercept of log K_F. The Freundlich isotherm can then be thought of as an adsorption reaction where the stoichiometry of the adsorbing species equals 1/n,

$$\overline{S} + 1/n\ (Cd_{tot}) \rightleftarrows \overline{SCd} \quad . \tag{32}$$

The mass action expression is then,

$$\frac{\overline{SCd}}{\overline{S}\,(Cd_{tot})^{1/n}} = K_F \quad . \tag{33}$$

There is no mass balance on surface sites and assuming an excess of sites with respect to the absorbate the activity of the free sites ($\overline{S}$) is set equal to one. There is one complication in use of the Freundlich isotherm in MINTEQ and that is in the stoichiometry of the adsorbing species. The stoichiometry of the adsorbing species in the mass action expression equals 1/n; however, the stoichiometry of the adsorbing species in the Cd mass balance equation equals one. Thus, to use the Freundlich isotherm in a geochemical model requires using separate stoichiometries for mass balance and mass action expressions.(a)

Equations (25) through (31) are written in terms of the total concentration of the adsorbate C_{tot} (or Cd_{tot}). Since C_{tot} involves all aqueous species, this formulation implicitly assumes that all species absorb with equal strength. There is abundant experimental evidence to support the hypothesis that only certain aqueous species react with the surface (Huang and Stumm 1973; Hohl and Stumm 1976; Davis and Leckie 1978). If C_{tot} is replaced with the activity of the aqueous species which dominates the adsorption reaction with the surface sites, say Cd^{2+} in the above examples, then the activity K_d is

$$K_d^{act} = \frac{\overline{SCd}}{\{Cd^{2+}\}} \quad . \tag{34}$$

(a) Only the UNIVAC and VAX versions of MINTEQ have this capability. Thus, the "activity" Freundlich isotherm cannot be used in the PDP 11/70 version unless 1/n ≈ 1.0.

The activity Langmuir equation is

$$S = \overline{SCd} = \frac{K_L^{act} \; S_T \; \{Cd^{2+}\}}{1 + K_L^{act} \; \{Cd^{2+}\}} \tag{35}$$

and the activity Freundlich equation is,

$$S = K_F^{act} \; \{Cd^{2+}\}^{1/n} \tag{36}$$

where { } denote the activity of the adsorbing species, in this example Cd^{+2} ion, in bulk solution.

The dependency of the 'concentration' K_d and isotherms on adsorbate aqueous complexation and ionic strength effects has been removed by using the 'activity' representation in Equations (34) to (36). K_d^{act} and the activity isotherms are thus applicable over a wider range of natural water compositions than the standard concentration representations.

A number of limitations remain, however. These descriptions of adsorption do not consider: 1) a charge balance on surface sites and adsorbed species; 2) electrostatic interactions between the adsorbing ion and the charged surface; and 3) reaction of the solid with aqueous constituents other than the adsorbate ion, e.g., H^+ and major supporting electrolyte anions and cations. The effect of these factors varies with changes in solution composition. Thus failure to include these factors in describing adsorption limits the range of applicability of that description. The surface complexation models described below incorporate these effects and are thus more generally applicable.

To use "activity" Langmuir/Freundlich isotherms in MINTEQ the following procedure (see MEXAMS - The Metals Exposure Analysis Modeling Systems) should be followed. For the activity Langmuir isotherm, include a surface site (i.e., SOH1 or SOH2) as a component and specify a mass total (equal to S_T) for that component. Then enter the adsorption reaction as a type II inserted species with an equilibrium constant of K_L^{act}, and set the adsorption model (IADS) to one. For the activity Freundlich isotherm, include a surface site (i.e., SOH1 or SOH2) as a component and give it a type III designation. Include the adsorption reaction as a type II inserted species with an equilibrium constant of K_F^{act}, and set the adsorption model (IADS) to one. Finally, set the stoichiometry of the adsorbing component to 1/n and set the stoichiometry in the "B" matrix to 1.0.(a)

Ion Exchange

Ion exchange reactions are modeled in the same way as in the geochemical model PHREEQE (Parkhurst et al. 1980). The reader is referred to this document for details; only a brief summary will be presented here.

Ion exchange reactions involve the exchange of ions of like charge on the solid surface. As an example, K^+ ion could exchange for Na^+ ion on the surface of the exchanger S,

$$Na^+ + \overline{KS} \rightleftarrows K^+ + \overline{NaS} \qquad (37)$$

(a) Only the UNIVAC and VAX versions of MINTEQ have this capability. Thus, the "activity" Freundlich isotherm cannot be used in the PDP 11/70 version unless $1/n \simeq 1.0$.

where $\overline{KS}$ represents exchanger bound potassium and $\overline{NaS}$ represents exchanger bound sodium.

MINTEQ, like PHREEQE, can model ion exchange reactions by maintaining a fixed activity ratio of the exchangeable species. Equations (38) and (39) present an example,

$$\frac{\{K^+\}\ \{\overline{NaS}\}}{\{Na^+\}\ \{\overline{KS}\}} = K_{ex} \tag{38}$$

$$K'_{ex} = K_{ex}\ \frac{\{\overline{KS}\}}{\{\overline{NaS}\}} = \frac{\{K^+\}}{\{Na^+\}} \quad . \tag{39}$$

The use of K'_{ex} assumes an infinite reservoir of exchanger at a constant solid phase composition [i.e., $\overline{KS}/\overline{NaS}$ remains fixed in Equation (39)]. This is equivalent to assuming that the concentration of exchangeable species on the surface is much greater than the concentration in solution. Therefore, even if the concentration of the exchangeable species in solution is changed, the activity ratio of the species in solution will re-adjust to the original fixed value due to the large reservoir of exchangeable species on the solid.

Surface Complexation Models

The "activity" Kd, "activity" Langmuir, "activity" Freundlich and ion exchange treatments described above all ignore electrostatic effects due to surface charge and the effect of solution chemistry on the solid. An electrical charge frequently exists on the surface of solid particles and creates an electrostatic potential which extends into solution. This

electrostatic potential can significantly influence the adsorption of charged species. In addition, pH and the concentration and composition of the electrolyte alter the distribution and availability of the surface hydroxyl groups which act as adsorption sites for the trace constituents, e.g., Cd. The surface complexation models described below include treatment of these effects.

Both of the surface complexation models of adsorption in MINTEQ, the constant capacitance model and the triple layer model, were developed for and have been primarily applied to crystalline oxides (Davis et al. 1978). These models have also been applied with considerable success to amorphous iron oxyhydroxides (Davis and Leckie 1978, Benjamin and Leckie 1981) and to clays (James and Parks 1982). Each model treats the oxide surface in contact with water as an array of hydroxyl groups designated as XOH, where X represent structural Si, Fe, Ti, Al, Mn or other atoms at the solid liquid interface (Figures 1 and 2). These hydroxyl groups or adsorption "sites" can be treated as ligands which: 1) have specific acid/base characteristics, and 2) form complexes with supporting electrolyte ions, metal ions or other ion-pairs in solution. Adsorption reactions, i.e., the coordination of these solute ions with surface hydroxyl groups, are treated by analogy with complexaton in bulk solution. Thus, for an assumed stoichiometry of reaction, an association (adsorption) constant can be used to describe the adsorption reaction. The description which follows for surface sites, XOH, can be generalized to include additional surface sites, SOH or TOH, whose acid/base or cation/anion coordination behavior differ from those of XOH.

Examples of surface equilibria for oxides are typically written for protonation and deprotonation reactions as

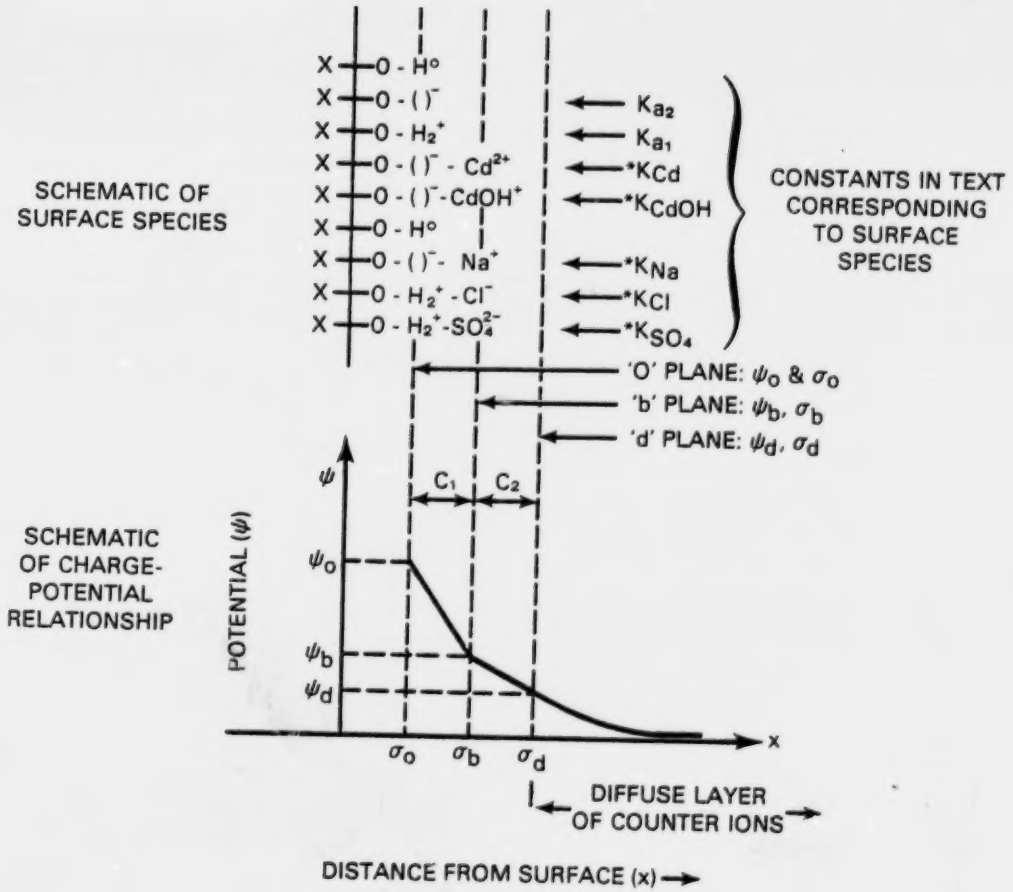


FIGURE 1. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Triple Layer Model. Brackets in the 'zero' plane indicate deprotonated surface sites.

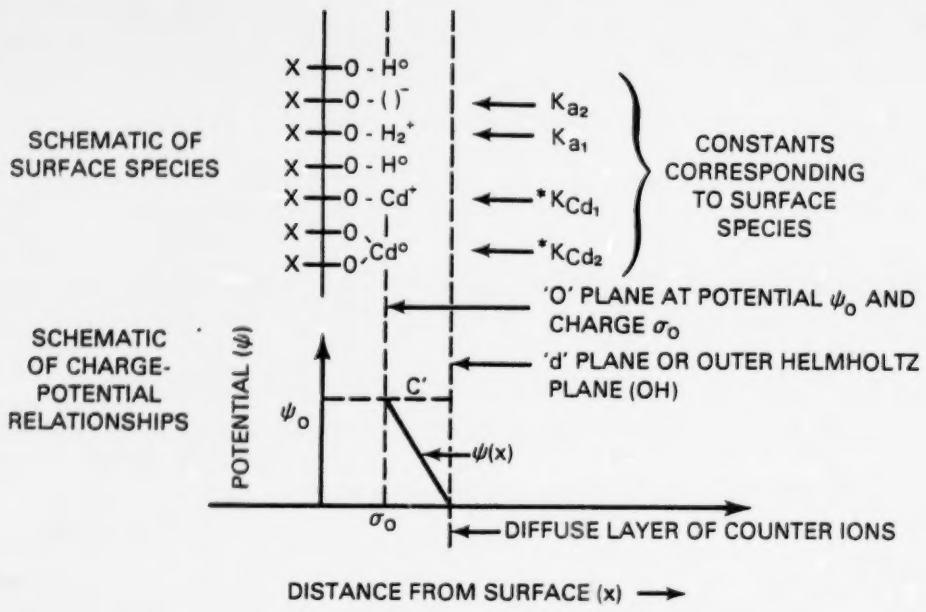


FIGURE 2. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Constant Capacitance Layer Model. Brackets in the 'zero' plane indicate deprotonated surface sites.

$$XOH + H_s^+ \rightleftarrows XOH_2^+,\ K_{a_1} = \frac{\{XOH_2^+\}}{\{XOH_2\}\ \{H^+\}_s} \tag{40}$$

$$XOH = XO^- + H_s^+,\ K_{a_2} = \frac{\{XO^-\}\ \{H^+\}_s}{\{XOH\}} \tag{41}$$

respectively, and for adsorption of a divalent cation, M^{2+}, as

$$XOH + M_s^{2+} \rightleftarrows (XO^- - M^{2+})^+ + H_s^+,\ {}^*K_M = \frac{\{XO^- - M^{2+}\}\ \{H^+\}_s}{\{XOH\}\ \{M^{2+}\}_s} \tag{42}$$

where K_{a_1}, K_{a_2}, are the first and second surface acidity constants, ${}^*K_M$ is an adsorption constant, { } represents the activity of surface species XOH, XO^-, XOH_2^+, and $(XO^- - M^{2+})$ in moles per liter and $\{\ \}_s$ represents the activity of an ion in the electrical double layer. The subscript "s" (H_s^+, M_s^{2+}) indicates that the H^+ and M^{2+} ions are in the electric double layer rather than in the bulk solution. The asterisk on the adsorption constant is a convention which indicates that the adsorption reaction is written in terms of the neutral site XOH rather than a deprotonated site XO^-.

A fundamental difference between adsorption reactions at the solid-solution interface and aqueous coordination reactions in bulk solution is that a variable electrostatic interaction energy exists between the charged adsorbing ion and the surface charge on the solid (Figures 1 and 2). A difference in chemical potential of the charged ion develops near the surface due to the electrostatic potential, ψ, produced by the surface charge, σ. Because of these nonideal interactions, the activities of ions approaching the

surface are modified by the electrical work necessary to bring them from the bulk solution to a specific adsorption plane within the electric double layer. The activities near the surface are related to the activities in bulk solution by an exponential Boltzman factor which is a function of potential. For any ion A^Z, this relation is,

$$\{A^Z\}_s = \{A^Z\}_{aq} \exp(-ZF\psi/RT)$$

where 's' and 'aq' refer to activities in the electrostatic double layer and in bulk solution, respectively, Z is the charge on ion A, F is Faraday's constant, R is the ideal gas constant in joules, T is the absolute temperature, and ψ is the electrostatic potential on the surface or at the designated adsorption plane within the double layer.

In MINTEQ, the activity coefficients for ions are calculated using the Debye-Huckel or Davies equations. Since no adequate theory exists for calculation of the activity coefficients for surface species, the activity coefficients in MINTEQ for all surface species are set equal to one and the activities, { }, of all surface species are replaced by concentrations, [ ].

The major differences betwen the constant capacitance and the triple layer models, as normally formulated, are: 1) the set of surface species considered (e.g., whether surface-electrolyte species are considered), and 2) the description of the electric double layer, i.e., the definition and assignment of ions to "mean" planes of adsorption within the double layer and the mathematical form of the surface charge-potential relation, $\sigma = f(\psi)$.

The mass action and mass balance equations in both the constant capacitance and the triple layer models are similar. For mathematical simplicity in MINTEQ, the Boltzman factor in the mass action equations for surface species, e.g.,

$$[XOH_2^+] = [XOH] \{H\}_{aq} \exp(-F\psi/RT) \qquad K_{a_1} ,$$

is treated as though it is just another chemical component. This new component is the coulombic or electrostatic component, $X(\sigma)$. From Equation (3) above, the mass balance equation used in MINTEQ to check convergence of each electrostatic component is,

$$Y(\sigma) = \sum_{i}^{m} a(i,\sigma)\, C_i - T(\sigma)$$

The electrostatic components are unique in that there is no measurable analytical value for total surface charge, $T(\sigma)$. A value for $T(\sigma)$ is calculated using the mathematical expression relating surface charge to potential, $\sigma = f(\psi)$, where $f(\psi)$ depends on the model of the electrical double layer used. Thus, $T(\sigma) = f(\psi)\, B$, where the factor B converts coulombs of charge per square meter into moles of charge per liter.

With this brief introduction, the constant capacitance and triple layer models will be described below for the case where adsorption occurs from a

solution containing Na^+, Cl^- and SO_4^{2-} as the major electrolyte ions and Cd^{2+} ion as the dilute adsorbate. Surface ligands consist of a single amphoteric surface site, XOH.

Constant Capacitance Model

With this model, all specifically adsorbed ions (H^+, OH^-, and Cd^{2+}) are considered to be located in the surface 'o' plane, contribute to the charge σ_o, and are subject to a potential, ψ_o, as shown in Figure 1. Ions which are not specifically adsorbed are excluded from the double layer and are assumed to be located in the diffuse layer. The dominant contribution to σ_o is from the potential determining ions H^+ and OH^-. It is assumed that the ions of the background electrolyte, Na^+, Cl^-, and SO_4^{2-} do not coordinate with the surface sites.

In the double layer, the surface charge-potential relationship used is the simple linear expression, $\sigma_o = C^1\psi_o$, where the capacitance of the double layer, C^1, is assumed to be constant. The surface hydrolysis and adsorption reactions together with the acidity and adsorption constants for the surface species as shown in Figure 1 are,

$$XOH + H_s^+ \rightleftharpoons XOH_2^+ \qquad K_{a_1} = \frac{[XOH_2^+]}{[XOH]\,\{H^+\}} \exp(\lambda\psi) \qquad (43)$$

$$XOH = XO^- + H_s^+ \qquad K_{a_2} = \frac{[XO^-]\,\{H^+\}}{[XOH]} \exp(-\lambda\psi_o) \qquad (44)$$

$$XOH + Cd_s^{2+} = (XO^- - Cd^{2+})^+ + H_s^+ \qquad {}^*K_{Cd_1} = \frac{[XO^- - Cd^{2+}]\,\{H^+\}}{[XOH]\,\{Cd^{2+}\}} \exp(\lambda\psi_o) \qquad (45)$$

$$(XOH)_2 + Cd_s^{2+} = ((XO^-)_2 - Cd^{2+})^0 + 2H_s^+, \quad {}^*K_{Cd_2} = \frac{[(XO^-)_2 - Cd^{2+}]\,\{H^+\}^2}{[(XOH)_2]\,\{Cd^{2+}\}} \qquad (46)$$

where $\lambda = F/RT$, $\{\ \}_{aq} = \{\ \}$ represents the activity in the bulk solution, $(XOH)_2$ and $(XO^-)_2$ represents two adjacent XOH and XO^- sites, respectively, acting as a single surface ligand,(a) and [ ] represents the concentration of surface species.

In MINTEQ, the surface sites, XOH, are treated as a chemical component, X(XOH). The mass balance equation for surface sites is,

$$Y(XOH) = \sum (\text{all surface sites}) - T(XOH) \qquad (47)$$

where

$$\sum \left(\begin{matrix}\text{all}\\ \text{surface sites}\end{matrix}\right) = [XOH] + [XO^-] + [XOH_2^+] + [XO^- - Cd^{2+}] + 2[(XO^-)_2 - Cd^{2+}]$$

is the sum of the concentrations of all of the surface sites as calculated from the mass action equations and T(XOH) is the analytical total concentration of surface sites in moles of sites per liter,

$$T(XOH) = N_S\ S_A\ C_S/N_A$$

Here, N_A is Avagadro's number, S_A is the specific surface area of the solid (m^2/g), C_S is the concentration of the solid in suspension (g/ℓ), and N_S is the analytically determined surface site density (number of sites/m^2).

In the case of the coulombic or electrostatic component, $X(\sigma_o)$, the equation describing the surface charge balance is,

(a) The UNIVAC and VAX versions, but not the PDP/11-70 version, of MINTEQ have the capability to model reactions with different stoichiometries in the mass action and mass balance equations.

$$Y(\sigma_o) = \sum (\text{charged species in 'o'}) - T(\sigma_o) \qquad (48)$$

where the total surface charge (i.e., the net concentration of charged sites in the 'o' plane in moles/ℓ) calculated from the mass action equations is,

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'o'}\end{matrix}\right) = [XOH_2^+] - [XO^-] + [XO^- - Cd^{2+}].$$

Since no analytical value of $T(\sigma_o)$ is available, the model dependent charge-potential relation is used to define $T(\sigma_o)$ in moles of charge per liter as,

$$T(\sigma_o) = \sigma_o B = C \psi_o B ,$$

where $B = (S_A C_S)/F$. By analogy with all other components in the formulation of the equilibriuim problem, the sum of charged surface species in Equation (48), calculated from the mass action equations, must equal the electrostatically calculated charge $T(\sigma_o)$, Equation (49), when the problem is solved.

When using the constant capacitance model, the coulombic component $X(\sigma_o)$ (PSIO in the MINTEQ code), must be designated as Type VI (see users manual MEXAMS - The Metals Exposure Analysis Modeling Systems) since it has no mass in aqueous solution. The input to MINTEQ requires: 1) an initial guess for the value of the electrostatic component, e.g., for $\psi > 0$, let $\log [X(\sigma_o)] = -1.0$; 2) the same value for the capacitance (C^1) for a given ionic strength and electrolyte as that used to derive the adsorption constants; 3) analytical values for the surface site density (N_S), the specific surface area (S_A) and the concentration of the solid in suspension (C_S); and 4) acidity and adsorption constants for surface hydrolysis and complexation reactions, determined experimentally for a given ionic strength and electrolyte composition.

For this model, in which coordination of the background electrolyte ions with surface sites is ignored, both the capacitance, C^1, and the adsorption constants depend on the type and concentration of the background electrolyte, and are applicable only at the ionic strength and for the specific electrolyte for which the adsorption data were obtained. However, for applications where the background electrolyte is fixed and the concentration of strongly coordinated electrolyte ions remain unchanged, use of the constant capacitance model requires less experimental characterization than is required by the triple layer model (described below). If, however conditions include variable concentrations of strongly coordinating electrolyte ions, use of the constant capacitance model would require new adsorption constants, derived from experimental adsorption data, for each set of conditions, reminicent of the early Kd approach previously described. For these conditions, the experimental characterization required by the triple layer is less extensive than that required by the constant capacitance model. This is a direct consequence of the triple layer model's inclusion of known electrolyte/surface reactions.

Triple Layer Model

This model treats the solid solution interface as being composed of two constant capacitance layers bounded by a diffuse layer (Figure 2). Specifically, adsorbed H^+ and OH^- ions are located in the surface 'o' plane, contribute to the surface charge ψ_o, and experience an electrostatic potential, σ_o. All other specifically adsorbed ions, including major electrolyte ions, are located in the 'b' or inner Helmholtz plane and are bound pairwise to oppositely charged surface sites by either a specific chemical or an electrostatic energy or both. These ions contribute to the charge, σ_b, and are subject to an electrostatic potential, ψ_b. The outer Helmholtz plane or the

'd' plane is the inner boundary of the diffuse region of nonspecifically bound counter ions. From theoretical considerations of monovalent electrolytes, the potential, ψ_d, in the 'd' plane is related to the total charge in the diffuse region, σ_d, by the Gouy-Chapman equation

$$\sigma_d = -(\varepsilon\varepsilon_o RIT)^{1/2} \sinh (F\psi_d/2RT) \quad ,$$

where ε and I are respectively, the dielectric constant and the ionic strength of the solution and ε_o is the permittivity of free space [8.85×10^{-12} $(\text{coulombs})^2$/joule-meter]. As an approximation in MINTEQ, the Gouy-Chapmay equation is also used for nonsymmetric electrolytes (charge on cation not equal to charge on anion).

Regions of constant capacitance, C_1 and C_2, separate the 'o' and 'b' planes and the 'b' and 'd' planes, respectively. In the context of this model of the solid-solution interface, the surface charge-potential relations, based on electrostatic considerations, are:

in the surface or 'o' plane,

$$\sigma_o = C_1(\psi_o - \psi_b) \tag{50}$$

in the 'b' plane,

$$\sigma_b = C_1(\psi_b - \psi_o) + C_2(\psi_b - \psi_d) \tag{51}$$

and in the 'd' plane

$$\sigma_d = C_2(\psi_d - \psi_b) \quad . \tag{52}$$

The expressions for the surface hydrolysis reactions are identical to those given in Equations (43) and (44) for the constant capacitance model. The adsorption reactions and constants for the other surface species shown in Figure 2 are,

$$XOH + Na_s^+ = (XO^- - Na^+)^0 + H_s^+$$

$$^*K_{Na} = \frac{[XO^- - Na^+]\ \{H^+\}}{[XOH]\ \{Na^+\}} \exp\left(-\lambda(\psi_o - \psi_b)\right)$$

$$XOH + Cl_s^- + H_s^+ = (XOH_2^+ - Cl^-)^0,$$

$$^*K_{Cl} = \frac{[XOH_2^+ - Cl^-]}{[XOH]\ \{CL^-\}\ \{H^+\}} \exp\left(\lambda(\psi_o - \psi_b)\right)$$

$$XOH + Cd_s^{2+} = (XO^- - Cd^{2+})^+ + H_s^+,$$

$$^*K_{Cd} = \frac{[XO^- - Cd^{2+}]\ \{H^+\}}{[XOH]\ \{Cd^{2+}\}} \exp\left(-\lambda(\psi_o - 2\psi_b)\right)$$

$$XOH + Cd_s^{2+} + H_2O = (XO^- - CdOH^+)^0 + 2H_s^+,$$

$$^*K_{CdOH} = \frac{[XO^- - CdOH^+]\ \{H^+\}^2}{[XOH]\ \{Cd^{2+}\}\{H_2O\}} \exp\left(-\lambda(\psi_o - \psi_b)\right)$$

$$XOH + (SO_4^{2-})_s + H_s^+ = (XOH_2^+ - SO_4^{2-})^-,$$

$$^*K_{SO_4} = \frac{[XOH_2^+ - SO_4^{2-}]}{[XOH]\{SO_4^{2-}\}\{H^+\}} \exp(\lambda(\psi_o - 2\psi_b))$$

Here, three electrostatic components, $X(\sigma_o)$, $X(\sigma_b)$, and $X(\sigma_d)$, in addition to the surface site component, X(XOH), are added to the normal set of chemical components describing the aqueous equilibrium problem. Within the content of the triple layer model, no bidentate surface species $[(XO^-)_2 - Cd^{2+}]$ have been considered. The set of surface species shown in Figure 2, although not necessarily unique, usually provides an adequate fit of experimental adsorption data for mono- and divalent cations and anions.

As a consequence of the inclusion of surface-electrolyte coordination reactions and the multiple layer structure of the interface, the acidity and adsorption constants defined for the triple layer model are 'intrinsic' constants, i.e., they are applicable over a wide range of pH, electrolyte and dilute adsorbate (Cd^{2+}) concentrations. However, experimental data over a wide range of chemical conditions is needed to determine these intrinsic constants (Davis et al. 1978; James et al. 1978; Balistrieri and Murray, 1979, 1981, 1982).

The mass balance equation for the surface site component, X(XOH), is identical to Equation (47) except that,

$$\sum\left(\begin{smallmatrix}\text{all}\\ \text{surface sites}\end{smallmatrix}\right) = [XOH] + [XOH_2^+] + [XO^-] + [XOH_2^+ - Cl^-] + [XO^- - Na^+]$$
$$+ [XO^- - Cd^{2+}] + [XO^- - CdOH^+] + [XOH_2^+ - SO_4^{2-}]$$

For the electrostatic components $X(\sigma_o)$ and $X(\sigma_b)$, the surface charge balance equations are, respectively,

$$Y(\sigma_o) = \sum (\text{charged species in 'o'}) - T(\sigma_o)$$

$$Y(\sigma_b) = \sum (\text{charged species in 'b'}) - T(\sigma_b) \quad ,$$

where

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'o'}\end{matrix}\right) = [XOH_2^+] + [XOH_2^+ \text{-}Cl^-] - [XO^-] - [XO^- \text{-}Na^+] - [XO^- \text{-}Cd^{2+}] - [XO^- \text{-}CdOH^+] + [XOH_2^+ \text{-}SO_4^{2-}]$$

and

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'b'}\end{matrix}\right) = [XO^- \text{-}Na^+] - [XOH_2^+ \text{-}Cl^-] + 2[XO^- \text{-}Cd^{2+}] + [XO^- \text{-}CdOH^+] - 2[XOH_2^+ \text{-}SO_4^{2-}]$$

The expressions for the T terms in these charge balance equations are $T(\sigma_o) = \sigma_o B$, and $T(\sigma_b) = \sigma_b B$, where B is a constant defined on Page 31 and σ_o and σ_b are defined by the Equations (50) and (51). The summations of the charged surface species in the 'o' and 'b' planes, calculated from mass action equations, must equal the electrostatically calculated charge, $T(\sigma_o)$, and $T(\sigma_b)$, respectively, when the equilibrium problem is solved. Since in this model there are no surface species assigned to the 'd' plane, the net charge in the diffuse layer, given by the Gouy-Chapman equation, must balance the electrostatic charge on the 'd' plane given by Equation (52). Thus, the charge balance equation for the electrostatic component, $X(\sigma_d)$, is,

$$Y(\sigma_d) = \left((-8\varepsilon\varepsilon_o RTI)^{1/2} \sinh(F\psi_d/2RT)\right) - \left(C_2(\psi_d - \psi_b)\right).$$

As equilibrium is approached during the numerical solution of the problem, $Y(\sigma_d)$ and the values of Y for all components approach zero.

When using the MINTEQ code to solve problems with the triple layer model, an initial guess is supplied as input to the code for the electrostatic components $X(\sigma_o)$, $X(\sigma_b)$, and $X(\sigma_d)$ (PSIO, PSIB, and PSID, respectively in MINTEQ). These components are given a Type VI designation (see the users manual MEXAMS - The Metals Exposure Analysis Modeling System) because they have no mass in aqueous solution. Other input data is similar to that required for the constant capacitance model except that a second capacitance, C_2, is needed. It should be noted that the K values defined for the triple layer model are not conditional constants, as is the case for the constant capacitance model, but are invariant with respect to adsorbate concentration below a surface loading threshold which depends upon the adsorbate/surface combination (Benjamin and Leckie 1981) and within the experimental range of pH and ionic strength for which they were determined.

SOLID PHASES

Saturated Indices

The saturation indices are used to describe the apparent closeness to equilibrium of a solid phase and the aqueous solution with which it is in contact. For solid dissolution reactions, saturation indices can be formulated in the following straight-forward manner:

$$SI_i = \log (K_r)_i - \log \left(\sum_{j=1}^{n} X_j^{a(i,j)} \right) \quad (53)$$

where SI_i is the saturation index for species (solid) i.

The thermodynamic data base in MINTEQ was taken from WATEQ3 (Ball et al. 1981). All reactions involving solid phases were written as dissolution reactions in WATEQ3. The mathematical formalism in MINTEQ requires all reactions to be written as formation reactions. Therefore, all equilibrium constants for solid phases in WATEQ3 were multiplied by minus one to convert the log K_r values to association reactions. This also resulted in Equation (53) being rewritten as

$$SI_i = \log (K_r)_i + \log \left[\sum_{j=1}^{n} X_j^{a(i,j)} \right] \quad (54)$$

The Stable Phase Assemblage

This section describes how MINTEQ selects the thermodynamically stable solids from the array of all considered solids (i.e., Type V solids) described in MEXAMS - The Metals Exposure Analysis Modeling System. The procedure described here has been modified only slightly from the original MINEQL model. Equation (55) is the mathematical relation which details whether a solid will be present (i.e., in equilibrium),

$$\log (K_r)_i + \log \sum_{j=1}^{n} X_j^{a(i,j)} < 0.0 \quad . \quad (55)$$

This inequality simply means that at equilibrium all solids being considered must either be in equilibrium or undersaturated. To solve this inequality, MINTEQ first ranks all considered solids by their tendency to precipitate. The tendency to precipitate is estimated by dividing the saturation index by the number of ions in the solid formation reaction. Dividing by the number of ions is necessary because the saturation indices are a function of the manner in which the chemical reaction is written. In the example below, doubling the reaction stoichiometry doubles the saturation index. If the activities of Ca^{2+} and SO_4^{2-} are 1×10^{-3},

$$Ca^{2+} + SO_4^{2-} \pm CaSO_4(s) \quad , \log K_r = 4.0 \; , \; SI = -2.0 \tag{56}$$

$$2\ Ca^{2+} + 2SO_4^{2-} \pm 2CaSO_4(s) \; , \log K_r = 8.0 \; , \; SI = -4.0 \tag{57}$$

Dividing the saturation indices by the number of ions in the solid helps to eliminate this effect.

After the solids have been ranked, MINTEQ, like MINEQL, precipitates the solid with the highest ranking (i.e., equilibrates the solution with that solid). The solids are ranked again and the process repeated until Equation (55) is satisfied. If the selection process makes a wrong choice and the mass of a previously precipitated solid becomes negative, then MINTEQ will redissolve the amount of that solid phase which was precipitated and continue.

Effect of Solids on pH and pE

The dissolution or precipitation of solid phases can alter the pH or pE of the solution. MINTEQ can model the changes in pH or pE as solids dissolve or precipitate as long as the appropriate mass totals are known.

The mass total for H^+ ion is determined by use of a form of the electroneutrality condition called the "proton condition" which is defined as the excess or deficiency of protons over the "zero level" species (Stumm and Morgan 1970). The "zero level" species in MINTEQ are the components. If anionic components are in their unprotonated forms and all cationic components are the uncomplexed ions, then the proton condition corresponds directly to a mass total for hydrogen ion or the total ionizable hydrogen (Morel and Morgan 1972). If components are chosen which contain H^+, for example HS^- or HCO_3^-, then the proton condition does not have the physical interpretation of a total mass of hydrogen ion but is still computationally valid.

To correctly predict changes in pH during precipitation or dissolution, the initial proton excess or deficiency first must be determined and then entered as the total mass of H^+. To obtain the initial proton excess or deficiency, one enters the measured pH and models the solution in MINTEQ without permitting precipitation or dissolution of solids. The computed aqueous mass of H^+ is then the initial proton excess or deficiency. When this value is entered as the total mass of H^+, MINTEQ will compute the correct pH as precipitation or dissolution occurs.

Electrons do not exist in aqueous solution. Therefore, to allow the pE to vary during the precipitation or dissolution of solids, the mass totals for all components of redox reactions must be known in the absence of solids. This may require an initial modeling run at fixed pH and pE to obtain the mass totals for all components of redox couples. Then one merely reenters the electron as

Type VI (see the Users Manual for MEXAMS - The Metals Exposure Analysis Modeling System) and remodels the solution in the presence of solids. MINTEQ will recompute the correct pE during precipitation or dissolution.

One of the advantages to this method of computing pH and pE is that H^+ and the electron are treated identically to all other components and the new pH and pE are recomputed along with all other component activities.

Initial Mass of Solid

MINTEQ can accept input of a starting mass of solid. The initially specified mass is added to the mass computed by MINTEQ from equilibrium constraints. If the mass of solid (i.e., computed mass plus initial mass) should become negative, then MINTEQ will dissolve the initially specified mass of solid by adjusting the mass totals in the solid formation reaction and removing the equilibrium constraint.

SECTION 5

NUMERICAL METHOD

MINTEQ utilizes a Newton-Raphson iterative technique to solve the series of simultaneous nonlinear equations relating component activity to total mass. The technique is identical to that described by Westall et al. (1976) except for modifications required for the constant capacitance and triple layer adsorption models.

Given an initial estimate of all X_j values, MINTEQ computes all C_i terms by Equation (1). The difference function (i.e., relaxed mass balance constraint) defined by Equation (3) is then computed. The problem now reduces to one of finding new estimates for the X_j values. In the Newton-Raphson iteration technique, a new estimate for the set of components X_j is computed by first differentiating the set of relaxed mass balance equations, Equation (3), with respect to the components, X_k, to obtain the elements Z_{jk} of the n x n Jacobian matrix,

$$Z_{jk} = \frac{\partial Y_j}{\partial X_k} = a(i,j)\ a(i,k)\ C_i/X_k \qquad (58)$$

where j and k vary from 1 to n and

$$\frac{\partial T_j}{\partial X_k} = 0$$

except for electrostatic components. For a derivation of Equation (58) see Westall et al. 1976. The correction vector $\underline{\Delta x}$ is computed from the matrix equation,

$$\underline{\underline{Z}}\ \underline{\Delta x} = \underline{y}$$

where $\underline{\Delta x}$ is equal to $(\underline{x}_N - \underline{x}_{N+1})$, N is the iteration number and $\underline{\underline{Z}}$ is the Jacobian matrix of partial derivatives just computed. The system of linear equations represented by this matrix equation is then solved by gaussian elimination, and a new set of X_j terms are computed.

The convergence criteria used in MINTEQ is identical to the criteria in MINEQL which is,

$$\frac{|Y_j|}{\max Y_j} < \varepsilon \qquad (59)$$

where max Y_j is the maximum of the terms comprising Y_j and ε equals 1×10^{-3} in MINTEQ. In the absence of solids, maximum Y_j equals T_j.

In the case of the constant capacitance and triple layer adsorption models $\partial T_j/\partial X_j \neq 0$ for the electrostatic components since the total charge depends upon the potential. The derivatives for the electrostatic terms have been computed by Westall (1979b) and are summarized in Table 1.

TABLE 1. DERIVATIVES FOR THE CONSTANT CAPACITANCE AND TRIPLE LAYER ADSORPTION MODELS (WESTALL 1979b)

Constant Capacitance Model

$$Z_{\psi_o,\psi_o} = \sum(\psi_o,\psi_o) + C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

Triple Layer Model

$$Z\psi_o,\psi_o = \sum (\psi_o,\psi_o) + C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

$$Z\psi_o,\psi_b = \sum (\psi_o,\psi_b) - C_1 \frac{RT}{FX_{\psi_b}} \cdot B$$

$$Z\psi_b,\psi_o = \sum (\psi_b,\psi_o) - C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

$$Z\psi_b,\psi_b = \sum (\psi_b,\psi_b) + (C_1 + C_2) \frac{RT}{FX_{\psi_b}} \cdot B$$

$$Z\psi_b\psi_d = - C_2 \frac{RT}{FX_{\psi_d}} \cdot B$$

$$Z\psi_d\psi_b = - C_2 \frac{RT}{FX_{\psi_d}} \cdot B$$

$$Z\psi_d\psi_d = [+8(\varepsilon\varepsilon_o RTI)^{1/2} \frac{F}{2RT} \cosh \frac{F\psi d}{2RT} + C_2] \frac{RT}{FX_{\psi_d}} \cdot B$$

Modified Line Search

The Newton-Raphson numerical method usually converges rapidly. Unfortunately, there are cases when the method does not converge. One of the most common instances of nonconvergence results from extremely poor starting estimates for the component activities. This frequently occurs for such components as Fe^{3+} or U^{4+} where the actual component activity is a small fraction of the mass total. In such cases the default starting estimate of one hundredth the mass total may be 20 or 30 orders of magnitude too high. Another common case of nonconvergence is when an aqueous solution contains two major components with essentially all of the mass of each component tied up in a common complex. In such cases, the ionic strength also varies with the major components activities and the numerical problem may become unstable.

For both of these cases of nonconvergence, the problem can usually be solved by making more accurate guesses for the component activities. Unfortunately, this may be a time consuming process. To help solve these problems, a modified line search has been included.

The modified line search is based on the fact that at convergence the component activities at the current iteration are approximately equal to the activities at the previous iteration (i.e., $X^N \simeq X^{N+1}$).(a) The line search uses this fact to modify the component activities (X_j terms) computed by the Newton-Raphson method. To understand the method, let X represent the component activity before Newton-Raphson correction and Y the value after Newton-Raphson correction. This means that at convergence, X = Y. The modified line search then simply monitors the progress of the iteration scheme and uses previous X-Y points to project new values for the component activities. The new values for

(a) The principal idea behind the modified line search was originally suggested by Dr. John R. Morrey, Battelle, Pacific Northwest Laboratories.

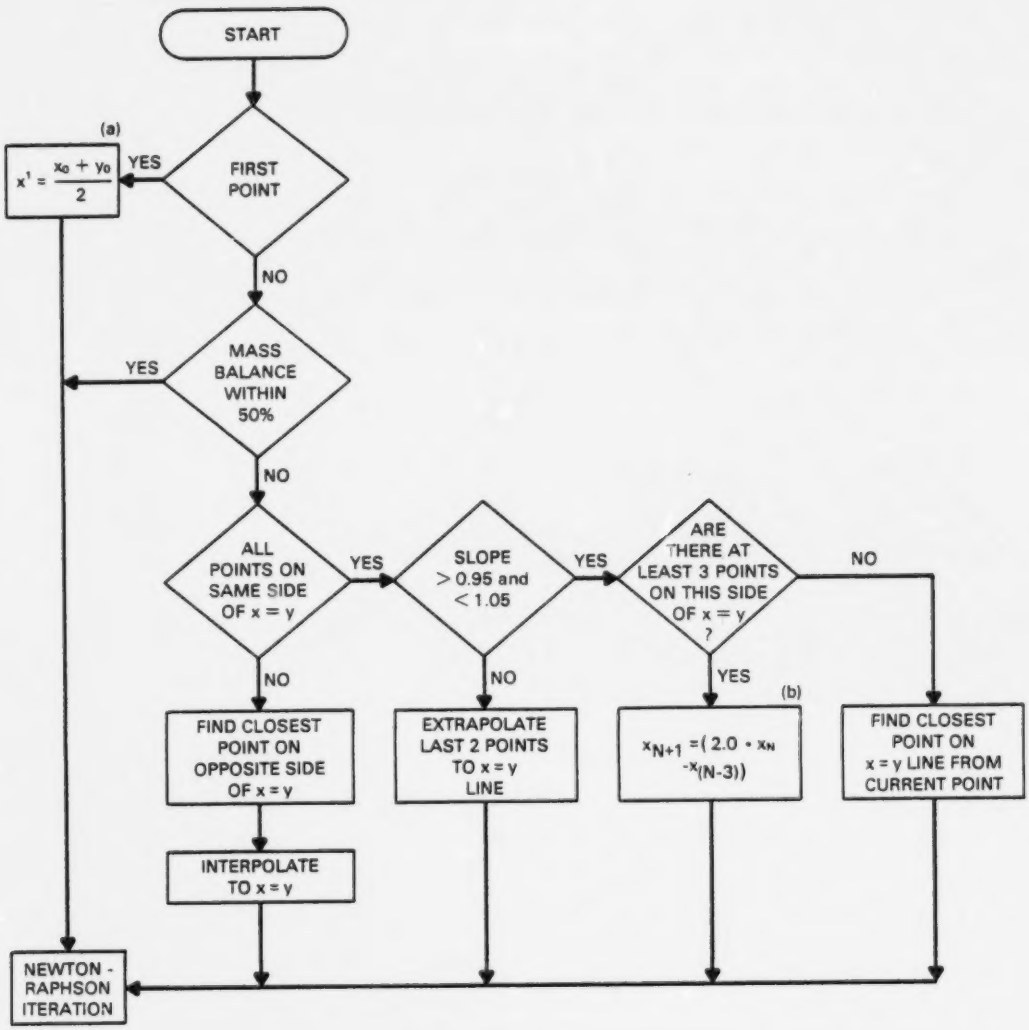
the component activities are obtained by either extrapolation or interpolation to the X = Y convergence line. The overall principal of the method is to refine the component activities to be close enough to the final solution values that the Newton-Raphson method will converge. The new values for the component activities are then used as the new starting estimates for the Newton-Raphson iteration. Figure 3 presents a logic diagram of the method.

An example convergence pattern for Fe^{3+} is shown in Figure 4. Figure 4 is a schematic of the following discussion. An initial estimate of the logarithm of the activity of Fe^{3+} (X_o) was made of -4.00. The Newton-Raphson iteration then produced a new estimate (Y_o) of -4.35. Since this is the first point, a new X_1 was computed,

$$X_1 = \frac{X_o + Y_o}{2} = -4.18 \quad .$$

Newton-Raphson iteration then yields Y_1 = -4.52. Since both points are on the same side of X = Y, and the computed slope is 0.96 and since there are only two points on this side of the line, the model chooses the closest point on the X = Y line [i.e., $X_2 = (X_1 + Y_1)/2.0 = -4.35$]. Newton-Raphson iteration produces Y_2 = -4.70. The point (X_2,Y_2) is on the same side of the X = Y line as the previous points, and the computed slope between the last two points equals 1.01. Now, however, there are three points on the same side of X = Y and the algorithm extrapolates, $X_3 = 2 * X_2^{(a)} = -8.70$. Newton-Raphson then returns a value of Y_3 = -9.00. Since this is also on the same side of the X = Y line and the slope is still approximately equal to one, the model

(a) In comparing Figure 3 X_{N-3} equals zero for the first extrapolation.


START
FIRST POINT
YES
(a)
$x^1 = \frac{x_0 + y_0}{2}$
NO
MASS BALANCE WITHIN 50%
YES
NO
ALL POINTS ON SAME SIDE OF x = y
YES
SLOPE > 0.95 and < 1.05
YES
ARE THERE AT LEAST 3 POINTS ON THIS SIDE OF x = y ?
NO
NO
NO
YES
(b)
FIND CLOSEST POINT ON OPPOSITE SIDE OF x = y
EXTRAPOLATE LAST 2 POINTS TO x = y LINE
$x_{N+1} = (2.0 \cdot x_N - x_{(N-3)})$
FIND CLOSEST POINT ON x = y LINE FROM CURRENT POINT
INTERPOLATE TO x = y
NEWTON - RAPHSON ITERATION

(a) ALL x VALUES ARE LOGARITHMS

(b) SUBTRACTING THE VALUE OF THE THIRD PREVIOUS ITERATION HELPS PREVENT OVER EXTRAPOLATION

FIGURE 3. Logic Diagram for Modified Line Search

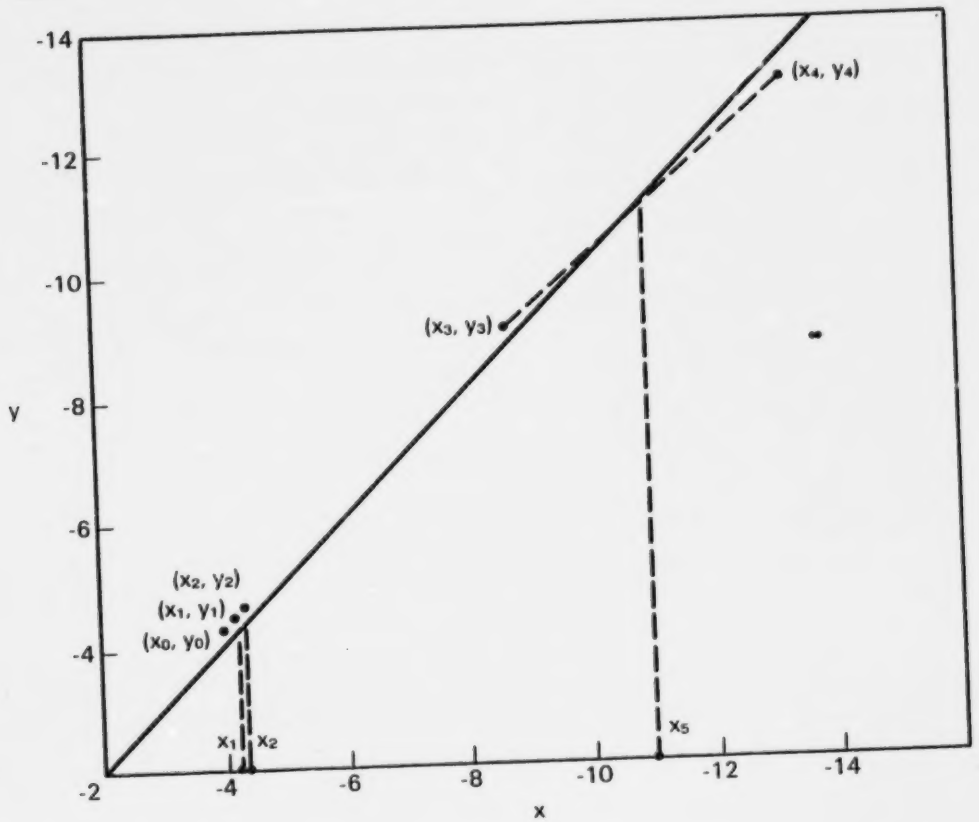


FIGURE 4. Example Convergence Pattern for Fe^{3+} Using the Modified Line Search. All values as logarithm.

extrapolates again $X_4 = 2X_3 - X_0 = -13.40$. Newton-Raphson then returns $Y_4 = -13.1$. The point (X_4,Y_4) is now on the other side of X = Y and the model interpolates a new point $[X_5 = (-slope \cdot X_4 + Y_4)/(1.0 - slope)] = -10.9$. Newton-Raphson then returns -11.1 which satisfies the mass balance criteria within 50% and the line search is complete.

It should be remembered that the line search utilized in MINTEQ was tested on only a few sample problems. The method is not intended to be used unless the user has been unable to get the Newton-Raphson method to converge. In such cases the method may prove useful but the users are advised that this option should be used at their own peril.

SECTION 6

THERMODYNAMIC DATA BASE

INTRODUCTION

The use of mass action expressions in MINTEQ requires the use of equilibrium constants ($\log K_r^o$) at a reference temperature of 298.15°K and zero ionic strength for entry into the data base. Equilibrium constants are extrapolated by MINTEQ to temperatures other than 298°K by use of the Van't Hoff relation which requires the enthalpy of reaction ($\Delta H^o_{r,298}$), when analytical expressions for $\log K_r^o$ are not available.

The equilibrium constants can be determined directly from solubility, potentiometric, ion exchange or other analytical methodologies (Rossotti 1981), or computed from calculated Gibbs free energies of reaction by the relationship,

$$\log K_{r,298} = \frac{\Delta G^o_{r,298}}{2.303\ RT}$$

where $\Delta G^o_{r,298} = \Sigma \Delta G^o_{f,298}$ (products) - $\Sigma G^o_{f,298}$ (reactants). The free energy of formation ($\Delta G^o_{f,298}$) is related to the heat of formation and entropy by,

$$\Delta G^o_{f,298} = \Delta H^o_{f,298} - 298.15\ \Delta S^o_{298} \quad .$$

Calorimetric measurements of the heat of solution and heat capacity can be used to compute, ΔH^o_f and ΔS^o_{298}, respectively. The enthalpy of reaction is readily computed,

$$\Delta H^o_{r,298} = \sum \Delta H^o_{f,298} \text{ (products)} - \sum \Delta H^o_{f,298} \text{ (reactants)} \quad .$$

Data for ΔH^o_f can be obtained from calorimetric measurements of the heat of solution or $\Delta H^o_{r,298}$ can be calculated from the experimentally determined variation of log K^o_r with temperature.

DATA IN MINTEQ

The selection of accurate and reliable thermodynamic data is extremely important to the reliability of chemical equilibrium model calculations (Nordstom et al. 1979). MINTEQ contains the WATEQ3 data base (Ball et al. 1981; Ball et al. 1980;[a] Truesdell and Jones 1974) which is the most thoroughly documented and evaluated thermodynamic data base used in any available geochemical model. However, when more recent and reliable experimental data, or data for reactions not present in the data base, become available, they should be included in the MINTEQ data base. The data base also contains some tabulated values for the minimum and maximum values for some equilibrium constants to assist in evaluating alternative thermodynamic data.

The thermodynamic data for MINTEQ will be listed in Appendix A. The included references refer to the selected values for log K^o_r and $\Delta H^o_{r,298}$. The

---

(a) A few clay minerals with either exchangeable cations in the chemical formula or variable component stoichiometrics as a function of pH were not included.

references do not give the primary source of the data but are intended as indexes to the tabulations which give the specific reactions and data sources.

ACCESSORY DATA

In addition to thermodynamic data, the MINTEQ data base also contains necessary supplementary data for each species. The data are summarized in Table 2. Most of these parameters have been previously described in this document or the accompanying User's Guide MEXAMS - The Metals Exposure Analysis Modeling System.

All Debye-Huckel parameters were taken directly from the WATEQ3 data base (Ball et al. 1981), the majority of which were in turn obtained from the tabulation in Truesdell and Jones (1974). Many of the Debye-Huckel parameters in the WATEQ3 data base for aqueous species of Cu, Mn and Zn were estimated.

TABLE 2. SUPPLEMENTARY DATA IN THE MINTEQ DATA BASE FOR EACH SPECIES

- Charge
- Gram formula weight
- Carbonate alkalinity factor
- Extended Debye Huckel parameters
- Name
- ID Number

REFERENCES

Baes, C. F., and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York, New York.

Balistrieri, L. S., and J. W. Murray. 1979. "The Surface of Goethite (αFeOOH) in Seawater." In Jenne, E. A., ed., Chemical Modeling in Aqueous Systems Speciation, Sorption, Solubility, and Kinetics. Am. Chem. Soc. Symposium, Ser. 93, p. 275-298.

Balistrieri, L. S., and J. W. Murray. 1981. "The Surface Chemistry of Geothite (αFeOOH) in Major Ion Sea Water. Amer. J. Sci. 281:788-806.

Balistrieri, L. S., and J. W. Murray. 1982. "The Adsorption of Cu, Pb, Zn, and Cd on Goethite from Major Ion Sea Water." Geochim. et Cosmochim. Acta. 46:1253-1265.

Ball, J. W., E. A. Jenne and D. K. Nordstrom. 1979. "WATEQ2: A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters." In Chemical Modeling in Aqueous Systems, ed. E. A. Jenne, pp. 815-835. Amer. Chem. Soc. Symp. Series 93.

Ball, J. W., E. A. Jenne and M. W. Cantrell. 1981. WATEQ3: A Geochemical Model with Uranium Added. U.S. Geol. Survey, Open File Report 81-1183.

Ball, J. W., D. K. Nordstrom and E. A. Jenne. 1980. Additional and Revised Thermochemical Data and Computer Code for WATEQ2--A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters. U.S. Geol. Survey Water Res. Invest. 78-116.

Benjamin, M. M., and J. O. Leckie. 1981. "Multiple-Site Adsorption of Cd, Cu,Zn and Pb on Amorphous Iron Oxyhydroxide." J. Colloid Interface Sci. 79:209-221.

Davies, C. W. 1962. Ion Association. Butterworths Pub., Washington D.C. 190 pp.

Davis, J. A., R. O. James, and J. O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: I. Computation of Electrical Double Layer Properties in Simple Electrolytes. J. Colloid Interface Sci. 63:480-499.

Davis, J. A., and J. O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions." J. Colloid Interface Sci. 67:90-107.

Garrels, R. M. and C. L. Christ. 1965. Solutions, Minerals, and Equilibria. Freeman, Cooper and Company, San Francisco, California.

Harvie, C. E., and J. H. Weare. 1980. "The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C." Geochemica et Cosmochimica. Acta. 44:981-987.

Helgeson, H. C. 1969. "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures." Amer. J. of Sci. 267:729-804.

Helgeson, H. C., J. M. Delany, H. W. Nesbitt and D. K. Bird. 1978. "Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals." Amer. J. Sci., 278-A.

Hohl, H., and W. Stumm. 1976. "Interaction pf Pb^{2+} with Hydrous γ-Al_2O_3." J. Colloid Interface Sci. 55:281-288.

Huang, C. and W. Stumm. 1973. "Specific Adsorption of Cations on Hydrous γ-Al_2O_3." J. Colloid Interface Sci. 43:409-420.

James, R. O., J. A. Davis and J. O. Leckie. 1978. "Computer Simulation of the Conductometric and Potentiometric Titrations of the Surface Groups on Ionizable Latexes." J. Colloid Interface Sci. 65:331-344.

James, R. O., and G. A. Parks. 1982. "Characterization of Aqueous Colloids by Their Electrical Double-Layer and Intrinsic Surface Chemical Properties." Surface Colloid Sci. 12:119-216.

Krupka, K. M., and E. A. Jenne. 1982. WATEQ3 Geochemical Model: Thermodynamic Data for Several Additional Solids. PNL-4276. Pacific Northwest Laboratory, Richland, Washington.

Lewis, G. N., and M. Randall. Revised by K. S. Pitzer and L. Brewer. 1961. Thermodynamics. Second Edition, McGraw-Hill Book Company, New York, New York.

Morel, F., and J. J. Morgan. 1972. "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems." Environ. Sci. Tech. 6:58-67.

Nordstrom, D. K., L. N. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, et al. 1979. "A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems." In Chemical Modeling in Aqueous Systems, ed. E. A. Jenne, pp. 857-892. Amer. Chem. Soc. Symp. Series 93.

Parker, V. B., D. D. Wagman and W. H. Evans. 1971. "Selected Values of Chemical Thermodynamic Properties. Tables for tne alkaline earth elements (elements 92 through 97 in the standard order of arrangement)." U.S. Natl. Bur. Standards Tech. Note 270-6.

Parkhurst, D. L., D. C. Thorstenson and L. N. Plummer. 1980. PHREEQE - A Computer Program for Geochemical Calculations. U.S. Geol. Survey Water Res. Invest. 80-96, 210 p.

Pitzer, K. S. 1973. "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations." Jour. of Phys. Chem. 77:268-277.

Pitzer, K. S., and J. J. Kim. 1974. "Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes." J. Am. Chem. Soc. 96:5701-5707.

Pitzer, K. S., and G. Mayorga. 1973. "Thermodynamics of Electroytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent." Jour. of Phys. Chem. 77:2300-2308.

Plummer, L. N., B. F. Jones and A. H. Truesdell. 1976. WATEQF - A FORTRAN IV Version of WATEQ, A Computer Program for Calculating Chemical Equilibrium of Natural Waters. U.S. Geol. Survey Water Res. Invest. 76-13.

Robie, R. A., B. S. Hemingway, and J. R. Fisher. 1978. "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. U.S. Geol. Survey, Bulletin 1452.

Rossotti, F. 1981. The Determination of Stability Constants. McGraw-Hill Co., Inc., New York, New York.

Schindler, P. W., B. Furst, R. Dick and P. U. Wolf. 1976. "Ligand Properties of Surface Silanol Groups: I. Surface Complex Formation with Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}. J. Colloid Interface Sci. 55:469-475.

Stumm, W., and J. J. Morgan. 1970. Aquatic Chemistry - An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley and Sons Inc., New York, New York.

Stumm, W., H. Hohl and F. Dalang. 1976. Interaction of Metal Ions with Hydrous Oxide Surfaces. Croat. Chem. Acta. 48:491-504.

Truesdell, A. H., and B. F. Jones. 1974. "WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters." U.S. Geol. Survey J. Res. 2:233-248.

Van Zeggeren, F., and S. H. Storey. 1970. The Computation of Chemical Equilibria. Cambridge Univ. Press, London, England.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm. 1968. "Selected Values of Chemical Thermodynamic Properties. Tables for the first thirty-four elements in the standard order arrangement." U.S. Natl. Bur. Standards Tech. Note 270-3.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm. 1969. "Selected Values of Chemical Thermodynamic Properties. Tables for elements 35 through 53 in the standard order of arrangement." U.S. Natl. Bur. Standards Tech. Note 270-4.

Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm and R. L. Hutall. 1981. "Selected Values of Chemical Thermodynamic Properties. Compounds of Uraniuim, Protactinium, Thorium, Actinium, and the Alkali Metals. U.S. Natl. Bur. Standards Tech. Note 270-8, U.S. Government Printing Office, Washington, D.C.

Wolery, T. J. 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals. The EQ3/6 Software Package. UCRL-52658, Lawrence Livermore Laboratory, Livermore, California.

Westall, J., 1979a. MICROQL I. A Chemical Equilibrium Program in BASIC. Swiss Federal Institute of Technology EAWAG, CH-8600, Duebendorf, Switzerland.

Westall, J. 1979b. MICROQL II. Computation of Adsorption Equilibria in BASIC. Swiss Federal Institute of Technology EAWAG, CH-8600, Duebendorf, Switzerland.

Westall, J. 1980. "Chemical Equilibrium Including Adsorption on Charged Surfaces." In Particulates in Water, ed. M. C. Kavanaugh and J. O. Leckie, pp. 33-44, Advances in Chem. Series 189.

Westall, J. C., J. L. Zachary and F. M. M. Morel. 1976. MINEQL, A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Tech. Note 18, Dept. Civil Eng., Massachusetts Institute of Technology, Cambridge, Massachusetts.

Westall, J., and H. Hohl. 1980. "A Comparison of Electrostatic Models for the Oxide/Solution Interface." Adv. Coll. Inter. Sci. 12:265-294.

Yates, D. E., S. Levine and T. W. Healy. 1974. "Site-binding Model of the Electrical Double Layer at the Oxide/Water Interface." Chem. Soc. Faraday I. 70:1807-1818.

APPENDIX A

REACTIONS AND THERMODYNAMIC DATA

This appendix contains a listing of the thermochemical data in MINTEQ. The references are for the equilibrium constants and enthalpy of reaction data.

Footnotes for Tables A-1, A-2, A-3.

(a) reaction written in terms of $H^+(aq)$ and $H_2O(aq)$.

(b) reaction written in terms of $CO_3^{2-}(aq)$ rather than $HCO_3^-(aq)$. For the reaction:

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$

log K = 10.33, ΔH_r^o = -3.617 taken from Ball et al. (1981) to maintain consistency with that data base. Log K is the same as in NBS 270 series.(a)

(c) reaction written in terms of $PO_4^{3-}(aq)$ rather than $HPO_4^{2-}(aq)$. For the reaction:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$$

log K = 12.346, ΔH_r^o = -3.53 taken from NBS 270-3 and identical to the values in Ball et al. (1981).

(d) reaction written in terms of $PO_4^{3-}(aq)$ rather than $H_2PO_4^-(aq)$. For the reaction:

$$2H^+ + PO_4^{3-} \rightleftharpoons H_2PO_4^-$$

log K = 19.553, ΔH_r^o = -4.52 taken from NBS 270-3(b) and identical to the values in Ball et al. (1981).

(e) reaction written in terms of Cu^{+1} rather than Cu^{+2} and e^-. For the reaction:

$$Cu^+ \rightleftharpoons Cu^{+2} + e^-$$

log K = -2.72 and ΔH_r^o = -1.65 from NBS 270-4, which is also the same values used in Ball et al. (1981).

(f) addition of WATEQ3 reactions 544 and 542 in Ball et al. (1981).

(g) reaction written in terms of $CO_3^{2-}(aq)$ rather than $H_2CO_3(aq)$. Thermodynamic data taken from NBS 270-3.

(h) reaction written in terms of $HS^-(aq)$ rather than $S^{2-}(aq)$. ΔG_f^o and ΔH_f^o for $HS^-(aq)$ from NBS 270-3.

(a) The NBS 270 series referred to here consists of NBS technical notes 270-3 (Wagman et al. 1968), 270-4 (Wagman et al. 1969), 270-6 (Parker et al. 1971), and 270-8 (Wagman et al. 1981).

(b) ΔG_f^o for $H_2PO_4^-(aq)$ in NBS 270-3 is in error and should be -270.17 kcal.

(i) reaction written in terms of $H_3AsO_4^0(aq)$ rather than $AsO_4^{3-}(aq)$. For the reaction:

$$AsO_4^{3-} + 3H^+ \rightleftharpoons H_3AsO_4^0$$

log K = 20.6, ΔH_r^o = -3.43 from NBS 270-3.

Data Sources for Tables A-1, A-2, A-3.

1. Ball et al. (1980)

2. Ball et al. (1981)

3. Plummer et al. (1976)

4. Truesdell and Jones (1974)

5. Recomputed by Krupka et al. (a) who reference Dongarra and Langmuir (1980) for the equilibrium constants.

6. Computed by Krupka et al. (a) who reference NBS 270-8 (Wagman et al. 1981).

7. Recomputed as part of this study using the data of Robie et al. (1978). The calculations are consistent with the accepted ancillary data of Krupka and Jenne (1981).

8. Recomputed as part of this study. ΔG_f^o and ΔH_f^o taken from Helgeson et al. (1978).

9. Recomputed as part of this study. $\Delta G_r^o = 65.9$ taken from Truesdell and Jones (1974) for:

   $$Al_2Si_4O_{10}(OH)_2 + 12\ H_2O \rightleftharpoons 2Al(OH)_4^- + 4H_4SiO_4^o + 2H^+.$$

   Reaction rewritten in terms of $Al^{3+}(aq)$ consistent with the ancillary data of Krupka et al. (1982).

10. Recomputed as part of this study. ΔG_f^o computed from log K in Baes and Mesmer (1976) written with $CO_2(g)$. ΔH_f^o taken from Robie et al. (1978). All ancillary data taken from NBS 270-3 except $Cu^{2+}(aq)$ and Cu(0) from Robie et al. (1978).

11. Krupka and Jenne (1982).

(a) Krupka, K. M., E. A. Jenne, and W. J. Deutsch (DRAFT). "Validation of the WATEQ4 Geochemical Model for Uranium." PNL-4333. Pacific Northwest Laboratory, Richland, Washington.

TABLE A.1. Thermochemical Data for Aqueous Complexes (Default Type II)

															REFERENCE	WATEQ REACTION NUMBER
2		1,000 893		1,000 180												
8937320	KUO2SO4 AQ	5.100		2,789											2	590
2		1,000 893		1,000 732												
8937321	KUO2SO4)2-2	6.100		4,183											2	591
2		1,000 893		2,000 732												
8935000	KUO2HPO4 AQ	-2.100		20,814											2	592
3		1,000 893		1,000 580		1,000 330										
8935001	KUO2HPO4)2	-11.599		42,988											5	---
3		1,000 893		2,000 580		2,000 330										
8935002	KUO2H2PO4+1	-5.700		22,643											2	594
3		1,000 893		1,000 580		2,000 330										
8935003	KUO2H2PO4)2	-16.5		44,70											2	595
3		1,000 893		2,000 580		4,000 330										
8935004	KUO2H2PO4)3	-28.6		66,245											2	596
3		1,000 893		3,000 580		6,000 330										
8937700	KUO2H3SIO4			-2,4											2	689
3		1,000 893		1,000 770		+1,000 330										
7317300	KS2	+2	11,4	-14,526											1	582
3		1,000 750		1,000 731		+1,000 330										
7317301	KS3	+2	10,4	-13,282											1	583
3		1,000 750		2,000 731		+1,000 330										
7317302	KS4	+2	9,7	-9,629											1	584
3		1,000 750		3,000 731		+1,000 330										
7317303	KS5	+2	9,5	-9,595											1	585
3		1,000 750		4,000 731		+1,000 330										
7317304	KS6	+2		-9,861											1	586
3		1,000 750		5,000 731		+1,000 330										

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TABLE A.1. (contd)

| | | |

TABLE A.1. (contd)

| | | |

TABLE A.1. (contd)

| | | |

TABLE A.1. (contd)

												REFERENCE	WATEQ REACTION NUMBER
2	1.000 10A	1.000 360											
1003001 KCU12 AQ	0.0000	3.5900							0.	0.0	0.0	366.2000	1	454
2	1.000 10A	2.000 360											
1001400 KCUHCO3 +	0.0000	12.400							1.	0.0	0.0	173.4170	1(B)	514
1.00 3	1.000 10A	1.000 140	1.000 350											
1001401 KCUCO3 AQ	0.0000	5.3990							0.	0.0	0.0	172.4090	1	515
2.00 2	1.000 10A	1.000 140												
1007321 KCO(SO4)2-2	0.0000	3.5000							-2.	0.0	0.0	286.4610	1	516
2	1.000 10A	2.000 732												
1001410 KCU FULVATE	0.0000	3.5000							0.	0.0	0.0	762.3990	1	529
2	1.000 10A	1.000 141												
1001420 KCU HUMATE	0.0000	3.5000							0.	0.0	0.0	2112.3990	1	530
2	1.000 10A	1.000 142												
6001000 KPBCL +	0.5000	1.0000							1.	0.0	0.0	242.6430	1	341
2	1.000 60A	1.000 180												
6001001 KPBCL2 AQ	1.0000	1.0000							0.	0.0	0.0	278.0960	1	342
2	1.000 60B	2.000 180												
6001002 KPBCL3 -	2.1700	1.6990							-1.	0.0	0.0	313.5490	1	343
2	1.000 60B	3.000 180												
6001003 KPBCL4 -2	3.5500	1.3000							-2.	0.0	0.0	349.0020	1	344
2	1.000 60B	4.000 180												
6001400 KPB(CO3)2-2	0.0000	10.6400							-2.	0.0	0.0	327.2080	1	345
4.00 2	1.000 60A	2.000 140												
6002700 KPBF +	0.0000	1.2500							1.	0.0	0.0	226.1880	1	346
2	1.000 60A	1.000 270												
6002701 KPBF2 AQ	0.0000	2.5600							0.	0.0	0.0	245.1860	1	347
2	1.000 60A	2.000 270												
6002702 KPBF3 -	0.0000	3.4200							-1.	0.0	0.0	264.1850	1	348
2	1.000 60A	3.000 270												
6002703 KPBF4 -2	0.0000	3.1000							-2.	0.0	0.0	283.1830	1	349
2	1.000 60A	4.000 270												
6003300 KPBOH +	0.0000	-7.7100							1.	0.0	0.0	224.1970	1	350
3	1.000 60A	1.000 2	-1.000 350											
6003301 KPB(OH)2 AQ	0.0000	-17.1200							0.	0.0	0.0	241.2040	1	351
3	1.000 60A	2.000 2	-2.000 350											
6003302 KPB(OH)3 -	0.0000	-26.0000							-1.	0.0	0.0	258.2120	1	352
3	1.000 60A	3.000 2	-3.000 350											
6003303 KPB4OH +3	4.0000	-6.3600							3.	0.0	0.0	431.3870	1	353
3	2.000 60A	1.000 2	-1.000 350											
6004920 KPBNO3 +	0.0000	1.1700							1.	0.0	0.0	269.1940	1	354
2	1.000 60A	1.000 492												
6007320 KPBSO4 AQ	0.0000	2.7500							0.	0.0	0.0	383.2510	1	355
2	1.000 60A	1.000 732												
6007300 KPB(HS)2 AQ	0.0000	15.2700							0.	0.0	0.0	273.3330	1	356
2	1.000 60A	2.000 730												
6007301 KPB(HS)3 -	0.0000	16.5700							-1.	0.0	0.0	306.4050	1	357
2	1.000 60A	3.000 730												
6005304 KPB3(OH)4+2	20.5000	-23.8000							2.	0.0	0.0	689.5990	1	358
3	3.000 60A	4.000 2	-4.000 350											
6001300 KPBOH +	2.0000	1.7700							1.	0.0	0.0	287.0940	1	455
2	1.000 60A	1.000 130												
6001301 KPBOH2 AQ	0.0000	1.4400							0.	0.0	0.0	366.9980	1	456
2	1.000 60A	2.000 130												
6003600 KPBI +	0.0000	1.9400							1.	0.0	0.0	334.0940	1	457
2	1.000 60A	1.000 360												
6003601 KPBI2 AQ	0.0000	3.1990							0.	0.0	0.0	460.9980	1	458
2	1.000 60A	2.000 360												
6001401 KPBCO3 AQ	0.0000	7.2400							0.	0.0	0.0	267.1990	1	468

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TABLE A.1. (contd)

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TABLE A.1. (contd)

								REFERENCE	WATEQ REACTION NUMBER
2.00 2	1.000 231	1.000 140				-2. 0.0 0.0	183.5640	1	210
2311401 KCU(CO3)2-2 0.0000	9.8300					1. 4.0 0.0	98.9990	1	211
4.00 2	1.000 231	2.000 140				0. 0.0 0.0	134.4520	1	212
2311000 KCUCL +	0.0500	0.4300				-1. 4.0 0.0	169.9050	1	213
2	1.000 231	1.000 180				-2. 5.0 0.0	205.3580	1	214
2311001 KCUCL2 AQ	10.5000	0.1600				1. 0.0 0.0	82.5440	1	215
2	1.000 231	2.000 180				1. 4.0 0.0	88.5530	1	216
2311002 KCUCL3 -	13.0900	-2.2900				0. 0.0 0.0	97.5600	1	217
2	1.000 231	3.000 180				-1. 0.0 0.0	114.5680	1	218
2311003 KCUCL4 -2	17.7800	-4.5900				-2. 0.0 0.0	131.5750	1	219
2	1.000 231	4.000 180				2. 0.0 0.0	161.1060	1	220
2312700 KCUP +	1.6200	1.2600				0. 0.0 0.0	159.6070	1	221
2	1.000 231	1.000 270				-1. 0.0 0.0	162.7610	1	222
2313300 KCUOH +	8.0000	-8.0000				1. 0.0 0.0	124.5630	1(B)	510
1	1.000 231	1.000 2	-1.000 330			0. 0.0 0.0	713.5460	1	527
23133e1 KCU(OH)2 AQ 0.0000	-13.6000					0. 0.0 0.0	2063.5450	1	528
1	1.000 231	2.000 2	-2.000 330			1. 4.0 0.0	100.8230	1	251
23133e2 KCU(OH)3 - 0.0000	-26.8990					0. 0.0 0.0	136.2760	1	252
1	1.000 231	3.000 2	-3.000 330			-1. 4.0 0.0	171.7290	1	253
23133e3 KCU(OH)4 -2 0.0000	-39.6000					-2. 5.0 0.0	207.1820	1	254
1	1.000 231	4.000 2	-4.000 330			1. 0.0 0.0	84.3680	1	255
2313e04 KCU2(OH)2+2 17.5390	-10.3590					1. 0.0 0.0	82.3770	1	256
1	2.000 231	2.000 2	-2.000 330			0. 0.0 0.0	99.3840	1	257
2317320 KCUSO4 AQ	1.2200	2.3100				-1. 0.0 0.0	116.3920	1	258
2	1.000 231	1.000 732				-2. 0.0 0.0	133.3990	1	259
2317300 KCU(HS)3 - 0.0000	25.8990					0. 0.0 0.0	117.8300	1	260
2	1.000 231	3.000 730				1.000 180			
2311402 KCUHCO3 + 0.0000	13.000					0. 0.0 0.0	131.5130	1	261
1.00 1	1.000 231	1.000 140	1.000 330			-1. 0.0 0.0	164.5850	1	262
2311410 KCU FULVATE 0.0000	6.1990					0. 0.0 0.0	161.4310	1	263
2	1.000 231	1.000 141							
2311420 KCU HUMATE 0.0000	6.1990								
2	1.000 231	1.000 142							
9501000 KZNCL +	7.7900	0.4300							
2	1.000 950	1.000 180							
9501001 KZNCL2 AQ	6.5000	0.4500							
2	1.000 950	2.000 180							
9501002 KZNCL3 -	9.5000	0.5000							
2	1.000 950	3.000 180							
9501003 KZNCL4 -2	10.9600	0.1990							
2	1.000 950	4.000 180							
9502700 KZNP +	2.2200	1.1500							
2	1.000 950	1.000 270							
9503300 KZNOH +	13.1990	-8.9600							
1	1.000 950	1.000 2	-1.000 330						
95033e1 KZN(OH)2 AQ 0.0000	-16.8990								
1	1.000 950	2.000 2	-2.000 330						
95033e2 KZN(OH)3 - 0.0000	-28.3990								
1	1.000 950	3.000 2	-3.000 330						
95033e3 KZN(OH)4 -2 0.0000	-41.1990								
1	1.000 950	4.000 2	-4.000 330						
9501004 KZNUMCL AQ 0.0000	-7.4800		-1.000 330						
4	1.000 950	1.000 2							
95073e4 KZN(HS)2 AQ 0.0000	14.9400								
2	1.000 950	2.000 730							
95073e1 KZN(HS)3 - 0.0000	16.1000								
2	1.000 950	3.000 730							
9507320 KZNSO4 AQ	1.5000	2.3700							

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TABLE A.1. (contd)

| | | |

TABLE A.1. (contd)

| | | |

TABLE A.1. (contd)

													REFERENCE	WATEQ REACTION NUMBER
3300020	K OH-			15.345	-13.990									
	2	1.000	2		-1.000	330								
3307700	KH3IO4	-		8.9550	-9.9300						-1.	5.5	0.0	17.0074	4	132
	2	1.000	770		-1.000	330					-1.	4.0	0.0	95.1070		
3307701	KH2IO4	-2		29.7140	-21.6190						-2.	5.4	0.0	94.0990	4	13
	2	1.000	770		-2.000	330					-2.	5.0	0.0	142.0760		
7702700	KSiF6	-2		-16.2600	30.1800										4	14
	4	1.000	770		6.000	270	4.000	330	-4.000	2	-1.	2.5	0.0	60.0250		
3300900	KH2BO3	-1		3.2240	-9.2400										1	201
	2	1.000	90		-1.000	330					-1.	2.5	0.0	60.0310		
0902700	KBF(OH)3	-		1.0500	-0.3990										4	25
	2	1.000	90		1.000	270					-1.	2.5	0.0	62.0220		
0902701	KBF2(OH)2	-		1.63500	7.63000										1	161
	4	1.000	90		2.000	270	1.000	2	1.000	330	-1.	2.5	0.0	64.0130	1(A)	162
0902702	KBF3OH	-		-1.5000	13.66700		2.000	2	2.000	330	-1.	2.5	0.0	66.0040	1(A)	163
	4	1.000	90		3.000	270	3.000	2	3.000	330	0.	0.0	0.0	17.0300	1(A)	164
3304900	KNH3	AQ		12.4000	-9.2520						-1.	5.0	0.0	114.1000	4	26
	2	1.000	490		-1.000	330					1.	6.5	0.0	41.3190	4	131
4907320	KNH4SO4	-		0.0000	1.1100						1.	4.5	0.0	43.3100	1(A)	24
	2	1.000	490		1.000	732					0.	0.0	0.0	84.3210	4	22
4903300	KNO3	+		15.435	-11.79						1.	4.0	0.0	85.3290	1	73
	3	1.000	490		1.000	2	1.000	330			0.	0.0	0.0	120.3730	1(B)	74
4902700	KNOP	+		0.6740	1.0200						-1.	5.4	0.0	119.2830	1	75
	2	1.000	490		1.000	270					1.	5.4	0.0	121.2990	4	123
4901400	KNaCO3	AQ		2.0220	2.9800						0.	0.0	0.0	120.2910	4(D)	124
2.00	2	1.000	490		1.000	140	2.000	330			1.	6.0	0.0	57.0870	4(C)	33
4901401	KNaHCO3	+		-2.430	11.400						1.	6.0	0.0	101.0970	4(A)	76
1.00	1	1.000	490		1.000	140	1.000	330			0.	0.0	0.0	100.0890	4(B)	77
4907320	KNaSO4	AQ		1.5490	2.2500						0.	0.0	0.0	136.1410	1	78
	2	1.000	490		1.000	732					0.	0.0	0.0	136.0590	1	23
4905800	KNaPO4	-		3.1000	6.5690						-1.	5.4	0.0	135.0510	4(C)	34
	2	1.000	490		1.000	580	1.000	330			1.	5.4	0.0	137.0670	4	121
4905801	KNaH2PO4	+		-1.140	21.066						1.	5.0	0	59.0780	4(D)	122
	3	1.000	490		1.000	580	2.000	330			-1.	5.4	0.0	82.9990	1	160
4905802	KNaHPO4	AQ		-0.230	15.220						0.	0.0	0.0	84.0070	4	69
	3	1.000	490		1.000	580	1.000	330							4(B)	70
1503300	KCaUO4	+		14.535	-12.540											
	3	1.000	150		1.000	2	-1.000	330								
1501400	KCaHCO3	+		1.7400	11.330											
1.00	1	1.000	150		1.000	140	1.000	330								
1501401	KCaLO3	AQ		4.0300	3.1500											
2.00	2	1.000	150		1.000	140										
1507320	KCaSO4	AU		1.4700	2.3490											
	2	1.000	150		1.000	732										
1505800	KCaHPO4	AU		-0.230	15.085											
	3	1.000	150		1.000	580										
1505801	KCaPO4	-		3.1000	6.4590											
	2	1.000	150		1.000	580	1.000	330								
1505802	KCaH2PO4	+		-1.140	20.960											
	3	1.000	150		1.000	580										
1502700	KCaF	+		3.1700	0.9400											
	2	1.000	150		1.000	580	2.000	330								
5001400	KnaCO3	-		0.7110	1.2600											
2.00	2	1.000	500		1.000	140										
5001401	KnaHCO3	AU		0.0000	10.0800											

TABLE A.2. Thermochemical Data for Redox Reactions and Gases (Default Type VI)

```
2812000 FE+3/FE+2   -10.0      13.032
     1      1.000 201     -1.000 200      1.000   1
4700020 KMNU4 =     176.0200  -127.0440
     4      1.000 470      4.000   2     -8.000 330    -5.000   1
4700021 KMNU4 =2    130.0200  -118.4400
     4      1.000 470      4.000   2     -8.000 330    -4.000   1
4914920 NU2/NU3     -43.76     28.57
     5      1.000 492     -1.000 491      2.000 330     2.000   1    -1.000   2
4984920 MN4/NU3    -187.055   119.077
     5     -1.000 492      1.000 492     -3.000   2    10.000 330     0.000   1
5680910 ASO3/ASO4   -38.915    19.444
     5      1.000  61      2.000   1      2.000 330    -1.000  60    -1.000   2
5980930 U+3/UO2+2   -14.63      8.420
     5      1.000 893      3.000   1      4.000 330    -1.000 890    -2.000   2
5918930 U04/UO2+2   -34.43      9.216
     5      1.000 893      2.000   1      4.000 330    -1.000 891    -2.000   2
592a930 UU2+/UO2+2   -3.30      2.765
     3      1.000 893      1.000   1     -1.000 892
0716700 MN03/MN+2    25.700    -25.507
     1      1.000 470     -1.000   1     -1.000 471
2302910 CU+1/CU+2     1.65       2.72
     1      1.000 251      1.000   1     -1.000 250
7307320 MO=/BUO-2   -60.14      33.66
     5      1.000 752      9.000 330      8.000   1    -1.000 730    -4.000   2
3301400 CH4(GAS)    -81.0      41.08
     6      1.000 140      8.000   1     10.000 330    -3.000   2      16.0432
3301401 CU2(GAS)    -0.55      18.16
     3      1.000 100      2.000 330     -1.000   2                   41.0100
3300021 02(AQ) SATO            -45.54
     3      2.000   2     -4.000 330     -4.000   1                   31.9988
3300022 02(AQ) CALL 155.03     -85.98
     3      2.000   2     -4.000 330     -4.000   1                   31.9988
0913305 AU0(OH)15+9 4          -17.229
     3      6.000 891     15.000   2    -15.000 330     9. 0.0  0.0  1683.2846
3300023 02(GAS)     134.63     -85.120
     3      2.000 002     -4.000 330     -4.000 801
```

REFERENCE	WATEQ REACTION NUMBER
1	1
1	179
1	180
1	400
1	127
1	487
2(F)	---
2	542
2	573
1	169
1	208
4(A)	90
4(B)	94
4(C)	137
4	136
4	151
2	550
4	93

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TABLE A.3. Thermochemical Data for Minerals and Solids (Default Type V or VI)

											REFERENCE	WATEQ REACTION NUMBER
8000100	URANINITE	10,630	4,700	.000	.000				270,0278		2	551
	1 -4,000 25a	1,000 691	2,000 2									
8000101	UO2 (am)	20,230	-,934	.000	.000				270,0278		2	552
	1 -4,000 25a	1,000 691	2,000 2									
8000102	UO2V (C)	101,235	3,384	.000	-3,000				1096,1106		2	553
	4 -10,000 25a	-2,000 1	4,000 691	9,000 2								
8000103	UO3H (C)	110,020	-21,107	.000	-34,569				842,0822		2	554
	4 -10,000 25a	-4,000 1	3,000 691	8,000 2								
8000104	UO2OH (C)	14,546	7,020	.000	.000				330,1121		2	555
	1 -4,000 25a	1,000 691	1,000 770									
8000105	UF4 (C)	10,900	10,046	.000	.000				314,0226		2	562
	1 1,000 691	4,000 270										
8000106	UF4,2,5H2O	,500	27,370	.000	.000				359,0606		2	563
	1 1,000 691	4,000 270	2,500 2									
8000107	UNPU(3)2,4H2O	-3,040	51,504	.000	.000				502,0486		2	571
	4 1,000 691	2,000 500	2,000 330	4,000 2								
8000108	NIAUTUNITE	2,270	53,906	.000	.000				584,0822		2	572
	4 1,000 691	1,000 150	2,000 500	2,000 2								
8000109	UO3 (C)	19,315	-7,719	.000	.000				286,0272		2	577
	1 -2,000 25a	1,000 693	1,000 2									
8000110	GUMMITE	43,015	-10,403	.000	.000				286,0272		2	578
	1 -2,000 25a	1,000 693	1,000 2									
8000111	B-UO2(OH)2	13,730	-5,564	.000	.000				304,0424		2	579
	1 -2,000 25a	1,000 693	2,000 2									
8000112	SCHOEPITE	12,045	-5,404	.000	.000				322,0576		2	580
	1 -2,000 25a	1,000 693	3,000 2									
8000113	RUTHERFORDIN	1,440	14,939	.000	.000				330,0370		2	584
	4 1,000 693	1,000 140										
8000114	(UO2)3(PO4)2	-94,980	49,037	124,134	.000				1000,0262		2	597
	7 1,000 691	2,000 500										
8000201	H-AUTUNITE	3,600	47,931	.000	.000				732,0144		2	598
	1 2,000 25a	2,000 693	2,000 500									
8000202	NA-AUTUNITE	,460	47,409	.000	.000				775,9780		2	599
	1 2,000 5na	2,000 693	2,000 500									
8000203	K-AUTUNITE	-5,800	46,244	.000	.000				808,2024		2	600
	1 2,000 41a	2,000 693	2,000 500									
8000204	URAMPHITE	-9,700	51,749	.000	.000				766,0756		2	601
	1 2,000 691	2,000 498	2,000 500									
8000205	SALEEITE	20,100	43,046	.000	.000				754,3104		2	602
	1 2,000 691	1,000 460	2,000 500									
8000206	AUTUNITE	14,340	43,927	.000	.000				778,0784		2	603
	1 2,000 691	1,000 150	2,000 500									
8000207	BA-AUTUNITE	13,050	44,457	.000	.000				817,6184		2	604
	1 2,000 691	1,000 800	2,000 500									
8000208	URANOCIRCITE	18,100	44,631	.000	.000				867,3384		2	605
	1 2,000 691	1,000 100	2,000 500									
8000209	BASSETITE	19,900	44,485	.000	.000				785,8454		2	606
	1 2,000 691	1,000 880	2,000 500									
8000210	TUROBENITE	15,900	45,279	.000	.000				793,5444		2	607
	1 2,000 691	1,000 231	2,000 500									
8000211	PHOSPHURANYLITE	11,000	44,365	.000	.000				937,1863		2	608
	1 2,000 691	1,000 600	2,000 500									
8000212	URANOPHANE	,000	-17,990	.000	.000				766,5176		2	610
	4 -8,000 25a	2,000 693	1,000 150	2,000 770								
9100300	UO2(OH)2	22,100	-12,369	.000	.000				394,0380		6	---
	2 1,000 691	2,000 492										
9100301	UO2(OH)2,4H2O	6,360	-4,851	.000	.000				430,0694		6	---

TABLE A.3. (contd)

											REFERENCE	WATEQ REACTION NUMBER
	3	1,000	6Y3	4,000	492	2,000	2			448,0840	6	---
5100302	UO2(NO3)2.3H2O	2,485		-3,642		,000		,000				
	3	1,000	6Y3	2,000	492	3,000	2			502,1500	6	---
5100303	UO2(NO3)2.6H2O	-4,770		-2,500		,000		,000				
	3	1,000	6Y3	2,000	492	6,000	2			78,0075	4(A)	140
2003000	AL(OH)3(A)	27,005		-10,388		-9,690		,000				
	1	1,000	3o	3,000	2	-3,000	330			148,0505	1	471
6003000	ALOHSO4	,000		3,030		3,590		3,070				
	4	-1,000	33o	1,000	3o	1,000	732	1,000	2	374,0616	1	472
6003001	AL4(OH)10SO4	,000		-22,700		,000		,000				
	4	-10,000	33A	4,000	3o	1,000	732	10,000	2	438,3597	1	338
6001000	ALUM K	-7,220		5,170		,000		,000				
	4	1,000	61o	1,000	3o	2,000	732	12,000	2	414,2141	4(A)	58
6001001	ALUNITE	-3,918		1,340		,000		,000				
	9	1,000	61o	3,000	3o	2,000	732	6,000	2	-6,000 330	4	17
6015000	ANHYDRITE	3,769		4,037		,000		,000		136,1416		
	2	1,000	15o	1,000	732						1	21
5015000	ARAGONITE	2,615		8,300		,000		,000		100,0894		
	2	1,000	15o	1,000	140						1	150
5040000	ANTIGITE	40,742		-9,000		,000		,000		196,6941		
	4	-2,000	33o	2,000	460	1,000	140	5,000	2		1	398
6010000	BAFE	-1,000		5,760		6,740		4,650		175,3368		
	2	1,000	14o	2,000	270						1	144
5010000	BARITE	-9,280		9,976		,000		9,775		233,4016		
	2	1,000	14o	1,000	732						4(A)	52
2003001	BOEHMITE	28,130		-8,970		-8,865		,000		59,9884		
	1	-3,000	33o	1,000	3o	2,000	2				4(A)	19
2040000	BRUCITE	15,840		-10,792		,000		,000		58,3268		
	3	1,000	46o	2,000	2	-2,000	330				1	12
5015001	CALCITE	2,585		8,475		8,560		,000		100,0894		
	2	1,000	15o	1,000	140						1	143
6040000	CELADITE	,670		6,465		,000		6,349		183,6816		
	2	1,000	60o	1,000	732						4	97
2077000	CHALCEDONY	-4,615		3,523		,000		,000		60,0848		
	2	-2,000	2	1,000	770						4(A)	20
8040000	CHRYSOTILE	32,485		-32,188		,000		,000		277,1349		
	4	-6,000	33o	3,000	46o	2,000	770	1,000	2		4(A)	29
8204000	CLINOCHRYSOTILE	44,015		-11,330		-10,972		-11,632		180,3964		
	4	-1,000	2	1,000	46o	1,000	770	-2,000	330		4	99
2077001	CRISTOBALITE	-5,500		3,587		,000		,000		60,0848		
	2	-2,000	2	1,000	770						4(A)	154
2003002	DIASPORE	24,630		-6,873		,000		,000		59,9884		
	3	-1,000	33o	1,000	3o	2,000	2				4(A)	28
6215000	DIOPSIDE	32,280		-19,000		,000		,000		216,5608		
	5	-2,000	2	1,000	15o	1,000	46o	2,000	770	-4,000 330	4	11
5015002	DOLOMITE	0,290		17,000		,000		,000		184,4106		
	3	1,000	17W	1,000	46o	2,000	140				1	340
6040000	EPIDOTE	-8,820		2,140		,000		,000		246,4807		
	3	1,000	90A	1,000	732	7,000	2				4(A)	36
6040003	EPIDOLITE(C)	47,260		-15,915		,000		,000		323,9313		
	4	-,5oo	2	2,000	46o	3,000	770	-4,000 330			4	112
2020100	FERRIHYDRITE	,000		-9,091		-1,557		-8,996		104,8692		
	3	-3,000	33A	1,000	28I	3,000	2				1	419
2020101	FE3(OH)8	,000		-20,822		-17,116		-20,103		297,6002		
	4	-8,000	33A	4,000	28I	1,000	20o	8,000	2		1	181
6120100	Fe(OH)2.7Cl.3	,000		3,000		,000		,000		110,4029		
1002000	FES PYT	,000		3,915		,000		,000		300 180	4	119

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TABLE A.3. (contd)

								REFERENCE	RATEQ REACTION NUMBER
[illegible]						395.8788		1	481
[illegible]						967.3e7d		1	396
[illegible]						78.8788		1	62
[illegible]						236.8234		4(A)	27
[illegible]						78.8837		1	51
[illegible]						86.8536		1	118
[illegible]						365.7393		1	111
[illegible]						289.7970		1	118
[illegible]						172.1722		4	18
[illegible]						58.4428		4	64
[illegible]						155.6919		4	188
[illegible]						353.8536		4	117
[illegible]						467.6736		4(A)	38
[illegible]						478.6978		1	284
[illegible]						494.8104		1	285
[illegible]						480.7320		1	337
[illegible]						87.9110		4	67
[illegible]						532.6521		4	98
[illegible]						159.6922		4	189
[illegible]						84.3214		4	10
[illegible]						231.5386		1	107
[illegible]						278.8157		1	339
[illegible]						322.1942		4	66
[illegible]						286.1428		4	60
[illegible]						138.3e75		1	149
[illegible]						417.2863		1	44
[illegible]						119.9750		4	114
[illegible]						60.0848		4	101
[illegible]						323.9300		4(A)	153

TABLE A.3. (contd)

											REFERENCE	RATED REACTION NUMBER

TABLE A.3. (contd)

														REFERENCE	WATEQ REACTION NUMBER
0	-10.000	25c	0.000	000	0.000	25	20.000	471	49.000	2	-0.000	470			
0010001	CaMoS4(s)		.000		.000		.000						464.1910	1	208
0	-10.000	25c	.000	150	0.000	471	12.000	2	-3.000	470					
0003000	Cu metal		-17.110		0.700		.000		0.000				63.5460	1	223
0	1.000	25c	1.000	1											
0103000	Cu(OH)2(c)		-9.904		6.700		.000		6.630				98.9990	1	224
0	1.000	25c	1.000	100											
0203000	CuO		12.170		-7.000		.000		.000				82.5444	1	225
0	1.000	25c	1.000	270											
0303000	Cu2O(c)		-0.295		1.550		1.010		.700				143.0914	1	226
0	-2.000	25c	2.000	230	1.000	2									
1003000	CuCl2(c)		-9.350		34.619		34.920		30.900				159.1560	1	227
0	-1.000	25c	2.000	230	1.000	730									
1003001	Cu(OH)Cl(c)		-7.001		33.920		.000		.000				154.9620	1	247
0	-1.000	25c	.000	231	1.000	230	1.000	730							
1003002	CuCl(c)		-6.535		31.070		.000		.000				143.2095	1	535
0	-1.000	25c	.050	231	1.500	230	1.000	730							
1003003	Cu2(OH)3Cl (c)		.000		37.079		.000		.000				121.0284	1	534
0	-1.000	25c	.000	231	.000	230	1.000	730							
1003100	Cu2(OH)3Cl (c)		.000		30.164		.000		.000				101.9646	1	533
0	-1.000	25c	.900	231	.200	230	1.000	730							
1003101	CuHSO4Cl(c)		-20.010		23.030		.000		22.170				95.6100	1	246
0	-1.000	25c	1.000	231	1.000	730									
0003000	Cu(OH)2		4.500		1.950		.000		.000				223.1536	1	228
0	2.000	25c	1.000	732											
1003000	CuHPO4(OH)2(c)		3.000		8.920		.000		6.000				151.3918	1	229
0	-0.000	25c	1.000	230	1.000	201	2.000	2							
0103100	Cu3(OH)4SO4(c)		10.320		-3.750		.000		-0.650				134.4520	1	238
0	1.000	231	4.000	100											
0003100	Cu(OH)		.000		9.050		7.050		9.010				123.5552	1	231
0	1.000	231	1.000	140											
0203100	Cu2O		15.320		.020		.000		.000				101.5428	1	232
0	1.000	231	2.000	470											
0203101	Cu2O, 2H2O		3.650		4.550		.000		.000				137.5732	1	233
0	1.000	231	2.000	270	2.000	2									
0203100	Cu(OH)2		19.250		-8.000		.000		-9.200				97.5606	1	234
0	-2.000	25c	1.000	231	2.000	2									
0103101	Cu4(OH)6SO4		10.690		-7.300		-7.240		-7.490				213.5669	1	237
0	-3.000	25c	4.000	231	3.000	2	1.000	100							
0103100	Cu3(OH)2(SO4)2		17.350		-9.000		.000		-9.510				240.1186	1	238
0	-2.000	25c	4.000	231	3.000	2	1.000	492							
0003100	CuSO4		.000		-0.090		.000		-0.900				354.7240	1	239
0	-0.000	25c	3.000	231	4.000	2	1.000	732							
0003101	CuSO4.5H2O		.000		-11.940		-11.150		-11.500				452.2854	1	240
0	-0.000	25c	4.000	231	6.000	2	1.000	732							
0003102	CuCl2		39.610		-10.790		.000		-17.000				470.3000	1	241
0	-0.000	25c	4.000	231	7.000	2	1.000	732							
0003101	Cu(NO3)2		13.260		-7.040		-7.350		-7.090				79.5454	1	242
0	-2.000	25c	1.000	231	1.000	2									
0003103	CuSeO3H2O		35.575		-11.930		.000		.000				239.1490	1	243
0	-2.000	25c	2.000	231	1.000	2	1.000	732							
7003100	Cu3(PO4)2		.000		36.050		.000		36.900				380.5000	1	244
0	3.000	231	2.000	500											
7003101	Cu3(PO4)2.3H2O		.000		35.160		.000		.000				434.6264	1	245
0	3.000	231	2.000	500	3.000	2									
0003100	CuSeO3		10.190		-3.010		-6.030		-3.020				159.0030	1	247
0	1.000	231	1.000	732											
0003103	CuHSeO3(OH)		-1.000		2.000		6.900		2.130				249.6790	1	248

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TABLE A.3. (contd)

										REFERENCE	WATEQ REACTION NUMBER
	1	1,000 231	1,000 732	5,000	2						
3003100	DIOPTASE	8,900	-8,580	,000	,000				157,6449	1	420
	3	-2,000 330	1,000 231	1,000 776							
3003100	CUPRICFERRITE	30,690	-5,880	-5,550	,000				239,2376	1	249
	6	-8,000 330	1,000 231	2,000 201	4,000	2					
3003100	CHALCOPYRITE	-35,480	35,270	,000	50,790				183,5150	1	250
	4	-2,000 330	1,000 231	1,000 200	2,000	730					
3003000	CUBE	-13,000	8,010	,000	,000				143,4500	1	459
	2	1,000 230	1,000 130								
3303000	CUI	-20,140	11,090	,000	,000				190,4505	1	460
	2	1,000 230	1,000 380								
3090000	IN METAL	36,700	-25,737	,000	-25,790				65,3000	1	265
	2	1,000 930	2,000 1								
0190000	INCL2	17,000	-7,010	,000	-7,000				136,2860	1	267
	2	1,000 930	2,000 100								
3090000	DOLOMITE	4,360	10,000	10,010	9,020				125,3092	1	268
	2	1,000 930	1,000 140								
[illegible]		1,000 930	1,000 140	1,000	2				[illegible]	1	269
0000000	INFO	10,000	1,920	,000	1,000				103,3760	1	270
	2	1,000 930	2,000 270								
0090000	Zeolite (A)	,000	-10,050	-10,000	-10,000				99,3900	1	271
	3	-2,000 330	1,000 930	2,000	2						
0090000	Zeolite (E)	,000	-10,000	,000	,000				99,3900	1	272
	3	-2,000 330	1,000 930	2,000	2						
0090000	Zeolite (G)	,000	-11,730	-11,320	-11,090				99,3900	1	273
	3	-2,000 330	1,000 930	2,000	2						
0090000	Zeolite (J)	,000	-11,710	-11,190	-11,000				99,3900	1	274
	3	-2,000 330	1,000 930	2,000	2						
0090000	Zeolite (K)	,000	-11,900	-10,950	-11,020				99,3900	1	275
	3	-2,000 330	1,000 930	2,000	2						
0190000	ZnSiO3(H2O)2	,000	-15,000	,000	,000				217,2369	1	276
	4	-3,000 330	2,000 930	3,000	2	1,000	100				
0190000	Zn2Si2O6(H2O)2	,000	-30,900	,000	,000				333,8644	1	277
	5	-4,000 330	3,000 930	4,000	2	2,000	100				
0090000	Zn4Si2O7(OH)2	,000	-7,500	,000	,000				260,8322	1	278
	6	-4,000 330	2,000 930	4,000	2	1,000	730				
0090000	Zn2SiO4(OH)2	,000	-20,900	,000	,000				459,6214	1	279
	6	-4,000 330	2,000 930	4,000	2	1,000	730				
0190000	Zn4Si2O7.6H2O	-5,510	-3,000	,000	,000				297,4610	1	280
	3	1,000 930	2,000 690	4,000	2						
0090000	Zn(OH)2(G)	,000	-11,310	-11,570	-11,000				81,3794	1	281
	3	-2,000 330	1,000 930	1,000	2						
0090000	ZnO(G)	21,000	-11,140	-10,990	-11,500				81,3794	1	282
	3	-2,000 330	1,000 930	1,000	2						
0090000	Zn3(OH)4SO4	60,000	-19,000	,000	,000				484,2540	1	283
	6	-4,000 330	3,000 930	4,000	730	1,000	2				
7090000	Zn3(PO4)2.4H2O	,000	32,000	,000	,000				458,1436	1	284
	5	3,000 930	2,000 300	4,000	2						
1090000	ZnO (H)	-3,670	9,050	,000	,000				97,4080	1	285
	3	-1,000 330	1,000 930	1,000	730						
1090000	ZnMn2O4(H)	-8,250	11,010	13,210	5,950				97,4080	1	286
	3	-1,000 330	1,000 930	1,000	730						
1090000	ZnFe2O4(H)	-5,060	9,000	10,180	8,350				97,4080	1	287
	3	-1,000 330	1,000 930	1,000	730						
0090000	ZnS(H)	19,070	-8,930	,000	,000				141,4637	1	288
	6	-2,000 330	-1,000 2	1,000	930	1,000	770				
0090000	ZnSiO3(H)	23,370	-13,330	-13,350	,000				220,0431	1	289

TABLE A.3. (contd)

| | | |

TABLE A.3. (contd)

									REFERENCE	NATEG REACTION NUMBER
								278,1400	1	362
								261,6514	1	363
								545,3154	1	364
								267,2694	1	365
								245,1960	1	366
								223,1990	1	367
								223,1990	1	368
								229,1400	1	369
								498,4000	1	370
								526,4570	1	371
								749,6364	1	372
								972,8330	1	373
								1350,3672	1	376
								1337,9213	1	377
								713,6000	1	378
								581,1391	1	379
								581,2170	1	380
								677,9869	1	381
								283,2837	1	382
								500,4031	1	383
								303,2576	1	384
								239,2004	1	385
								239,1900	1	386
								462,3982	1	387
								685,5976	1	388
								261,2196	1	389
								259,0001	1	390
								506,0709	1	391
								775,0336	1	392

TABLE A.3. (contd)

REFERENCE	RATED REACTION NUMBER
1	393
1	465
1	466
1	467
1	394
1	410
1	411
1	412
1	413
1	414
1	415
1	416
1	417
1	418
1	437
1	438
1	439
1	440
1	441
1	442
1	443
1	444
1	445
1	446
1	---
1	---
1	---
1	---
1	---

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TABLE A.3. (contd)

												REFERENCE	WATEQ REACTION NUMBER
5	1,000 500	1,000	30	3,000 770	-4,000 330	-4,000	2						
8450003 ANALBITE		20,000	-3,566	,000	,000						262,2250	7	***
5	1,000 500	1,000	30	3,000 770	-4,000 330	-4,000	2						
8641000 MUSCOVITE		59,340	-12,990	,000	,000						398,3110	7	***
4	1,000 410	3,000	30	3,000 770	-10,000 330								
8641001 ANNITE		65,720	-23,490	,000	,000						511,8900	8	***
5	1,000 410	3,000	200	1,000 30	3,000 770	-10,000 330							
8415001 ANORTHITE		70,660	-25,430	,000	,000						278,2110	7	***
4	1,000 150	2,000	30	2,000 770	-6,000 330								
8603002 PYROPHYLLITE		,000	1,596	,000	,000						360,3138	9	***
4	2,000 30	4,000	770	-4,000 2	-6,000 330								
8415002 LAUMONTITE		50,450	-14,460	,000	,000						470,4410	8	***
4	1,000 150	2,000	30	4,000 770	-8,000 330								
8415003 NAINAKITE		63,150	-18,870	,000	,000						434,4110	8	***
5	1,000 150	2,000	30	4,000 770	-8,000 330	-2,000	2						
5023101 MALACHITE		15,610	5,180	,000	3,940						221,1162	10	***
4	2,000 231	2,000	2	1,000 140	-2,000 330								
5023102 AZURITE		23,770	16,920	,000	,000						344,6716	10	***
4	3,000 231	2,000	2	2,000 140	-2,000 330								
3006000 ARSENOLITE		-14,330	2,001	2,859	2,728						395,6824	1	497
2	4,000 60	-6,000	2										
3006001 CLAUDETITE		-13,290	3,065	,000	3,021						395,6824	1	498
2	4,000 60	-6,000	2										
4306000 AS13		-1,875	-4,155	,000	,000						455,6547	1	499
4	1,000 60	3,000	380	3,000 330	-3,000	2							
1006000 ORIPMENT		-82,890	60,971	,000	46,004						246,0350	1	500
4	2,000 60	3,000	730	3,000 330	-6,000	2							
1006001 REALGAR		-30,545	19,747	26,574	,000						106,9855	1	501
5	1,000 60	1,000	730	2,000 330	1,000	1	-3,000	2					
3006100 AS2O5		5,485	-6,999	,000	-9,478						229,8400	1	488
2	2,000 61	-3,000	2										
5295000 ZN(BO2)2		,000	-8,290	,000	,000						150,9893	1	266
4	-2,000 2	-2,000	330	1,000 950	2,000	90							
5216000 CD(BO2)2		,000	-9,840	,000	,000						198,0188	1	314
4	-2,000 2	-2,000	330	1,000 160	2,000	90							
5260000 PB(BO2)2		5,600	-7,610	,000	,000						292,8093	1	361
4	-2,000 2	-2,000	330	1,000 600	2,000	90							
7047001 MNHPO4(C)		,000	25,400	,000	,000						150,9174	1(C)	194
3	1,000 470	1,000	580	1,000 330									
7060006 PBHPO4		,000	23,900	,000	,000						303,1693	1(C)	374
3	1,000 600	1,000	580	1,000 330									
7060007 PB3(PO4)2		,000	44,500	,000	,000						811,5125	1(C)	375
2	3,000 600	2,000	580										
8073100 SULFUR		4,200	2,110	,000	,000						32,0640	1(H)	402
3	1,000 730	-1,000	330	-2,000 1									
7203000 ALASO4,2H		,000	-4,000	,000	,000						165,9006	1(I)	489
4	1,000 30	1,000	61	2,000 2	-3,000	330							
7215300 CA3(ASO4)2OH		,000	-22,300	,000	,000						586,1700	1(I)	490
4	3,000 150	2,000	61	4,000 2	-6,000	330							
7223100 CU3(ASO4)2OH		,000	-6,100	,000	,000						576,5680	1(I)	491
4	3,000 231	2,000	61	2,000 2	-6,000	330							
7226100 FEASO4,2H		,000	-,900	,000	,000						230,7967	1(I)	492
4	1,000 261	1,000	61	2,000 2	-3,000	330							
7247000 MN3ASO42H		,000	-12,500	,000	,000						586,7746	1(I)	493
4	3,000 470	2,000	61	8,000 2	-6,000	330							
7254000 NI3(ASO4)2H		,000	-15,700	,000	,000						459,1707	1(I)	494
4	3,000 540	2,000	61	8,000 2	-6,000	330							
7260000 PB3(ASO4)2		,000	-5,000	,000	,000						899,4079	1(I)	495

TABLE A.3. (Contd)

														REFENENCE	MATEQ REACTION NUMBER
5	3,000 000	2,000 61	-6,000 330												
7295000 ZN3AS0422,5H		,000	-13,650	,000	,000								510,9862	1(I)	496
4	3,000 950	2,000 61	2,500 2	-6,000 330											
7218000 BA(AS04)2		-2,640	8,910	,000	,000								689,8582	1(I)	541
3	3,000 100	2,000 61	-6,000 330												
2015000 LIME		40,265	-32,797	0	0								0	11	---
5	-2,000 330	1,000 150	1,000 002												
2015001 PORTLANDITE		30,690	-22,675	0	0								0	11	---
3	-2,000 330	1,000 150	2,000 002												
2024000 MUSTITE		24,846	-11,687	0	0								0	11	---
3	-2,000 330	0,947 280	1,000 002												
2046001 PERICLASE		30,135	-21,510	0	0								0	11	---
3	-2,000 330	1,000 460	1,000 002												
3029001 MERCYNITE		78,360	-27,162	0	0								0	11	---
4	-6,000 330	1,000 280	2,000 030	4,000 002											
3046000 SPINEL		69,089	-36,333	0	0								0	11	---
4	-8,000 330	1,000 460	2,000 030	4,000 002											
3046001 MAG-FERRITE		66,639	-16,765	0	0								0	11	---
4	-8,000 330	1,000 460	2,000 281	4,000 002											
4250000 CRYOLITE		-10,984	31,498	0	0								0	11	---
3	1,000 030	3,000 500	6,000 270												
8215002 WOLLASTONITE		19,498	-12,996	0	0								0	11	---
4	-1,000 002	-2,000 330	1,000 770	1,000 150											
8215003 P-WOLLSTANIT		21,066	-13,046	0	0								0	11	---
4	-1,000 002	-2,000 330	1,000 770	1,000 150											
8015001 CA-OLIVINE		54,695	-37,649	0	0								0	11	---
3	-4,000 330	1,000 770	2,000 150												
8015002 LARNITE		57,238	-39,141	0	0								0	11	---
3	-4,000 330	1,000 770	2,000 150												
8015007 CA3SIO5		106,335	-73,867	0	0								0	11	---
4	-6,000 330	1,000 770	3,000 150	1,000 002											
8015003 MONTICELLITE		49,421	-30,272	0	0								0	11	---
4	-4,000 330	1,000 770	1,000 150	1,000 460											
8015005 AKERMINITE		76,445	-47,472	0	0								0	11	---
5	-1,000 002	-6,000 330	2,000 770	2,000 150	1,000 460										
8015004 MERWINITE		107,111	-66,543	0	0								0	11	---
4	-8,000 330	2,000 770	1,000 460	3,000 150											
8441000 KALSILITE		28,919	-12,836	0	0								0	11	---
4	-4,000 330	1,000 770	1,000 030	1,000 410											
8441001 LEUCITE		22,885	-6,423	0	0								0	11	---
5	-2,000 002	-4,000 330	2,000 770	1,000 030	1,000 410										
8441002 MICROCLINE		12,389	-3,616	0	0								0	11	---
5	-4,000 002	-4,000 330	3,000 770	1,000 030	1,000 410										
8441003 H SANIDINE		14,252	-1,062	0	0								0	11	---
5	-4,000 002	-4,000 330	3,000 770	1,000 030	1,000 410										
8450004 NEPHELINE		33,204	-14,218	0	0								0	11	---
4	-4,000 330	1,000 770	1,000 030	1,000 500											
8015006 GEHLENITE		116,125	-56,822	0	0								0	11	---
5	-10,000 330	2,000 030	1,000 770	2,000 150	3,000 002										
2026103 LEPIDOCHROCIT		0	-1,371	0	0								0	11	---
3	-3,000 330	1,000 281	2,000 002												
8650000 NA-NONTRONIT		0	14,304	12,122	16,886								0	11	---
6	-7,320 330	-2,680 002	0,330 030	2,000 281	0,330 500	3,670 770									
8641002 K-NONTRONITE		0	15,549	12,765	18,334								0	11	---
6	-7,320 330	-2,680 002	0,330 030	2,000 281	0,330 410	3,670 770									
8615000 CA-NONTRONIT		0	20,869	19,057	22,722								0	11	---
6	-7,320 330	-2,680 002	0,330 030	2,000 281	0,167 150	3,670 770									
8646005 MG-NONTRONIT		0	20,569	19,015	22,165								0	11	---
6	-7,320 330	-2,680 002	0,330 030	2,000 281	0,167 460	3,670 770									
0															